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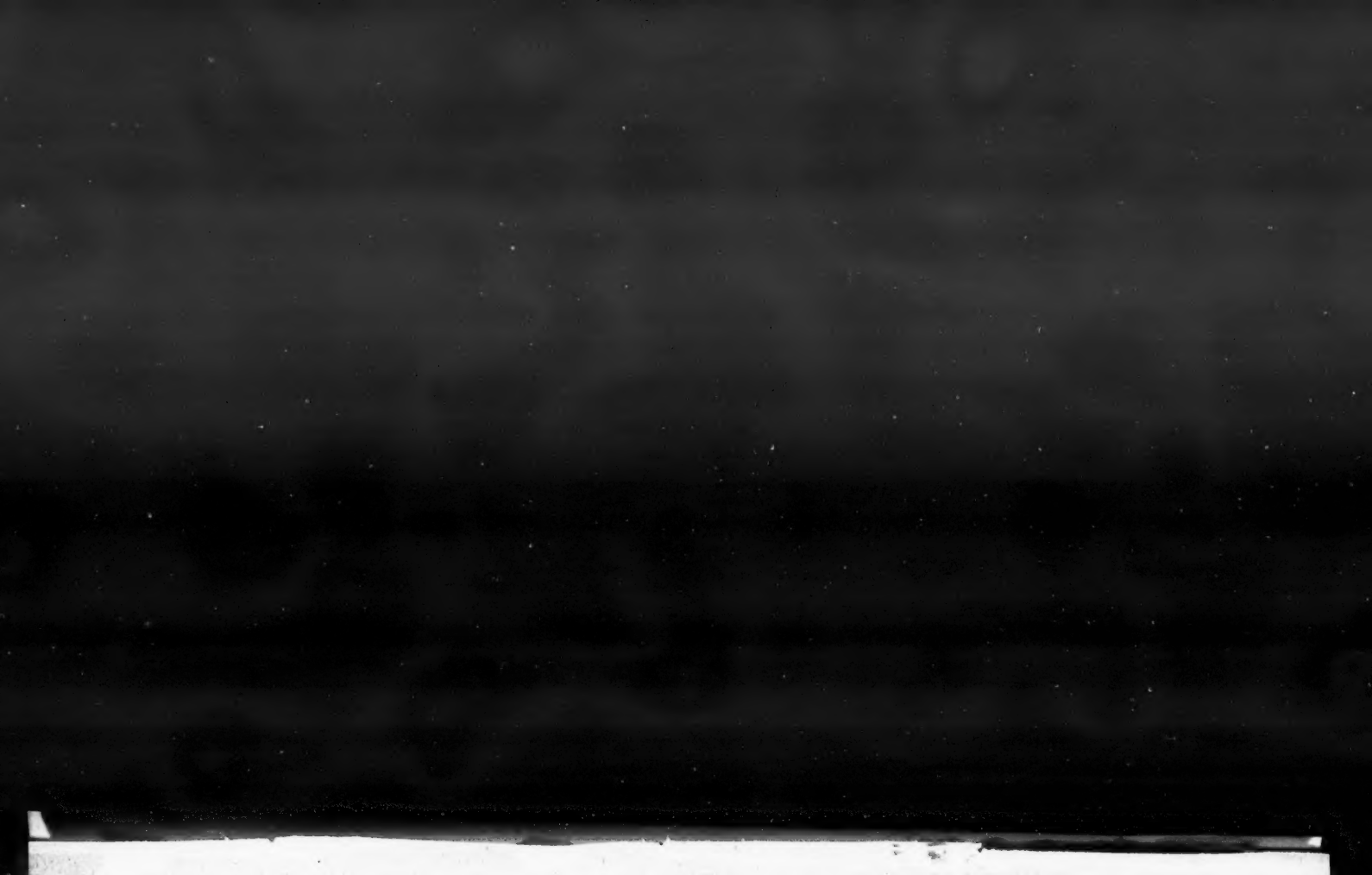

James D. Dana

JAMES DWIGHT DANA.

JAMES DWIGHT DANA, Professor of Geology and Mineralogy in Yale College and for fifty years one of the editors of this Journal, died suddenly at his residence in New Haven, Connecticut, on the fourteenth of April, 1895, at the age of eighty-two years and two months.

He was born in Utica, New York, on the twelfth of February, 1813. His father, James Dana, was of New England birth, having moved to Utica from his parents' home in Massachusetts. He was a successful business man and died in 1860 at the age of eighty. His mother was Harriet Dwight, daughter of Seth Dwight of Williamsburgh, Massachusetts.

The strong inborn taste for science was shown in early years, and he was fond of relating his pleasant experiences at the Bartlett Academy in Utica, when, as a boy of twelve, he studied chemistry with his associates, sharing with them the responsibility of preparing the experiments and delivering to the others the formal lectures. At the same time, frequent excursions after minerals with his companions served to give a special direction to his scientific interests and thus helped to determine the department in which his first work was to be done when maturity had developed his powers. These excursions were led by Mr. Fay Edgerton, the excellent instructor in Natural Science, and extended to distant parts of the State and also to neighboring States; one excursion into Vermont was remembered with much delight.

To the opportunities afforded by the early training in science, that have been alluded to, and to the interest it excited, Professor Dana ascribed much of the success that he afterwards attained. One of his schoolmates, closely associated with him in the Bartlett Academy, was S. Wells Williams, for many years missionary in China and in his later life again a colleague

among the corps of instructors at New Haven. A number of others, who subsequently rose to prominence, were among those who shared the inspiration of Mr. Edgerton's instruction. It is also of interest that Dr. Asa Gray, a close friend from early days, took Mr. Edgerton's place in the school in 1831.

In 1830, attracted by the name and reputation of Professor Silliman, he came to New Haven and entered the class of 1833 of Yale College, then in its Sophomore year. He was a faithful student, but those were days of a rigid course of study, chiefly in the classics, affording little to appeal to a mind with a strong bent for the methods and facts of science. It is not surprising, therefore, that though obtaining a good place on the honor list he did not make a brilliant record for general scholarship. He was, moreover, at a disadvantage because of insufficient training in the ancient languages, felt especially by one entering after the close of the first year of the course. It should be stated, however, that during his undergraduate life, he attained distinction in mathematics, a subject for which he always had decided aptitude. During this time he made much progress in science, especially in his favorite study of Mineralogy. In Botany also he took great interest; during his College life he made a large collection of the plants of the New Haven region, and a printed list of the local flora, carefully checked and annotated by him, is still preserved.

For music he had throughout his life a strong love, and when in College he devoted much attention to it, being on one occasion president of the Beethoven singing society, and for a time the leader of the college choir. He also made some attempts at musical composition. One of these was the music for an ode to the Ship "Peacock" of the Exploring Expedition (see p. 332), written by the Surgeon, Dr. J. C. Palmer; both gentlemen found a source of recreation and pleasure in their joint musical and poetical work during the voyage. It is interesting to note that many years later when upwards of seventy and unable because of ill health to write, he came back to his music and derived much comfort from working at it.

The influence of the elder Silliman, then at the height of his powers and reputation, did much to decide him to devote him-

self permanently to science, as will be seen in the events that followed. It is a point of interest also, as proving how deep his natural love of science was, that from home he obtained no encouragement whatever in turning his studies in this direction; indeed, from the time of graduation he assumed the entire burden of his own support. To his father's practical mind scientific pursuits did not commend themselves, but it should be stated that he lived to take a cordial interest and pride in his son's success.

Mr. Dana left New Haven in August, 1833, somewhat in advance of graduation, to avail himself of the opportunity offered of a cruise in the Mediterranean, as instructor in mathematics to the midshipmen of the United States Navy. In this capacity he visited a number of the seaports of France, Italy, Greece and Turkey, while on the "Delaware" and the "United States." This trip, lasting about fifteen months, brought much pleasure and profit. He was cut off for a time from his favorite minerals, but he occupied his leisure hours on shipboard with working out, by methods of his own, many of the more intricate problems of mathematical crystallography. Some notes of the voyage also mention the fact that he was interested in the study of the geology of the island of Minorca and that he made some collections in Natural History while there. It will be observed that the first paper recorded in the Bibliography, which follows this notice, is an account of the condition of Vesuvius in July, 1834, at the time of his visit; this was published in this Journal in 1835.

In 1836, Mr. Dana returned to New Haven and for two years remained there, occupied for more than a year as assistant in Chemistry to Professor Silliman. It was during this period that he published his first important contribution to Science,—the System of Mineralogy, a volume of 580 pages. This was in May, 1837, hardly four years after his graduation from College and when a young man of twenty-four; notwithstanding his youth, the work is that of a thoroughly mature and well informed scholar. A little earlier (1835) his notes mention the fact that he had constructed a set of crystallographic models in glass, probably the first time this had been attempted.

While at New Haven, another opportunity came to him for travel and observation, this time as Mineralogist and Geologist

to the Exploring Expedition then about to be sent by the government of the United States to the Southern and Pacific oceans under the command of Commodore Charles Wilkes. The invitation, when first received in 1836, was refused, but on the urgent solicitation of Dr. Asa Gray, then expecting to go as Botanist, the decision was reconsidered and finally the position accepted. He was disappointed in failing to have the companionship promised, but subsequent events brought the two men closely together and Dr. Gray remained an intimate personal friend and highly valued scientific associate until his death in 1888.

The expedition, consisting of five ships, sailed in August, 1838, and Mr. Dana was connected with it until June, 1842. The route was briefly as follows. First to Madeira, then to Rio Janeiro, down the coast and through the Straits of Magellan, after passing which, while on board the "Relief" he nearly suffered shipwreck off Noir island, the ship remaining three days and nights in extreme peril; in the same storm one of the smaller accompanying vessels was lost. Then to Chili, Peru and across to the Paumotus, to Tahiti and the Navigator islands; then to New South Wales, where the naturalists remained while Commodore Wilkes went into the Antarctic; then to New Zealand, the Fiji islands, where two of the officers were murdered by the natives; to the Sandwich islands, the Kingsmill Group, the Caroline islands and thence north to the coast of Oregon. Here, near the mouth of the Columbia river, the "Peacock," the ship to which he had been assigned, was wrecked, entailing the loss of all his personal effects as well as many of his collections. He was, then, one of the party that crossed the mountains near Mt. Shasta and made their way down the Sacramento river to San Francisco. In his report of the expedition he states that the geological features indicated the probable presence of gold. This was six years before the discovery of gold in California, and rich mines have since been discovered in the region the party went over. At San Francisco the party were taken aboard the "Vincennes" and the homeward journey was made by way of the Sandwich islands, Singapore, the Cape of Good Hope and St. Helena. The arrival in New York was on June 10, 1842.

The opportunities of this long journey to many of the most interesting points in the world were such as have been offered to few young men of his years and could never come again. The stimulus of the multitude of new facts to observe and of new forms of life to collect and study was extraordinary, and the effect of these four years upon the attainments of his subsequent life was profound. Of the beauties of the life in the sea about the coral islands and of that of the tropics in general he never tired of speaking; his lecture on "Coral Islands" delivered in later years to many generations of college students, contained a vivid description of the scenes he enjoyed so much.*

It is interesting to note here, that a few years before the American expedition was in the Pacific, the British ship "Beagle," having the naturalist Darwin on board, had sailed through much of the same region. The theory explaining the formation of the coral atoll by gradual subsidence, first advanced by Darwin (1842), was also independently worked out to a large extent by the American naturalist.† The latter showed, moreover, that the reef-building corals lived only in water of at least 68 degrees Fahrenheit, which proved that the distribution of corals depended on the temperature of the water.

As already stated, Mr. Dana was first appointed in the field of Geology, and his observations and deductions are given in a large quarto volume of 756 pages with a folio atlas of 21 plates (1849). Later, however, in part because of the return of one of his colleagues to the United States, he assumed charge also of the Crustacea and Zoöphytes. These combined departments gave full scope to his zeal and industry. The results of his work in this department of Zoölogy include a *Report on Zoöphytes*, a quarto volume of 741 pages, with a folio atlas of 61 plates (1846); also a *Report on Crustacea*, in two quarto volumes aggregating 1620 pages (1853) and accompanied by a folio atlas of 96 plates (1854). These three reports will be more particularly spoken of later, but it may be mentioned here that a large part of the drawings of the plates in both works were made by his own hand.

* This subject is presented in somewhat popular form in the work entitled "Corals and Coral Islands," first published in 1872.

† A brief discussion of this theory is given on a later page of this number (p. 426); it was one of the last subjects on which he wrote.

In June, 1842, Mr. Dana returned to the United States and for the next thirteen years devoted his chief energies to the study of the material collected on the expedition and to the preparation of the reports mentioned. His labors, however, were not limited to this field, for during the same period, he prepared and issued three editions of the System of Mineralogy (1844, 1850, 1854) and two editions of the Manual of Mineralogy (1848, 1857), besides writing numerous papers for this and other scientific periodicals.

From 1842 to 1844, he resided in Washington, and later in New Haven. On June 5, 1844, he married Miss Henrietta Frances, third daughter of Professor Benjamin Silliman, whose assistant he had been in 1836–37, and with whom he was from this time closely associated in scientific work.

The labor on the material from the Exploring Expedition was carried forward with the enthusiastic zeal of an earnest student with a new world open before him, and who was but little restrained by the thought that injury to health was possible. How severe and intense the labor of this period was will be evident from the fact that a few years after the last Report was published, Mr. Dana's health broke down, and so completely that though he lived thirty-five years after this and accomplished a wonderful amount of scientific work, life was from this time ever a struggle and, not always with success, against physical disability.

In 1846, Mr. Dana was made an editor of this Journal, associated with Professor Benjamin Silliman, who had founded it twenty-eight years before, and with his son, Professor Benjamin Silliman, Jr. His labors in connection with the Journal continued until the close of his life.

In 1850, Mr. Dana was appointed Professor of Natural History in Yale College, and in 1864 the title was changed to that of Professor of Geology and Mineralogy. His duties as instructor, however, he did not take up until 1855, but, after this date, with some interruptions due to ill health, as more particularly noted later, his active connection with the college continued until 1890. It is perhaps interesting to add that just before his appointment to Yale in 1850, he had been invited to a similar position at Cambridge, Massachusetts, in connection

with Harvard College, but by the prompt action of a generous friend in the Yale Faculty in providing the necessary funds, he was induced to remain in New Haven on the "Silliman Professorship." This gentleman, who is still living, remained throughout the life of Mr. Dana one of his closest friends.

In 1859, as already noted, long continued over-work brought a break-down of a serious character and from which he never fully recovered. The nervous prostration was very complete at first, and even a period of nearly a year abroad, from Oct. 1859 to August 1860, seemed to have little result in the way of restoration. Although later some degree of health gradually came back, he was always subject to the severest limitations until the end of his life. Only those immediately associated with him could appreciate the inexorable character of these limitations and the self-denial that was involved not only in restricting work and mental effort, but also in avoiding intercourse with other men of science and friends in general, in which he always found the greatest pleasure.

Little by little the power for work was restored and by husbanding his strength so much was accomplished that, besides other writing, he was able to bring out in 1862 the first edition of his Manual of Geology, and in 1864 the Text Book of Geology, and four years later his last and most important contribution to Mineralogy, the fifth edition of the System.

This last great labor, extending over four years, was followed by a turn of ill health of an alarming character and from which restoration was again very slow. The years that immediately followed were filled with the same quiet labor, on geological investigations in the field, the writing of original papers and books, the editorial work of this Journal, and his duties as a college instructor. They were remarkably productive years, notwithstanding the difficulties contended against, notably renewed illness in 1874 and 1880, as will be seen by reference to the Bibliography. A large number of important papers were published, chiefly in this Journal: new editions of the Manual of Geology were issued in 1874 and 1880; of the Text Book in 1874 and 1883; while a new geological volume called "The Geological Story briefly told," was issued in 1875 and one on "Corals and Coral Islands" in 1872.

The years from 1887 to 1890 include the time when he most nearly threw off the limitations of ill health. In the summer of 1887, accompanied by his wife and youngest daughter, he revisited the Sandwich Islands, the acquaintance of which he first made in 1840, when on the Exploring Expedition. This was, indeed, the first long journey made except that to Europe in search of health in the years of 1859–60, since the expedition returned in 1842. He was led to make this journey* because of the interest aroused in discussing the phenomena connected with the eruption of the volcano of Kilauea on the island of Hawaii. The journey brought the keenest pleasure, not only that due to revisiting the Sandwich Islands themselves but also that of making the acquaintance of a number of interesting places in the western United States. Although travel had ordinarily been too severe a tax since his health gave out, this journey of ten weeks extending over ten thousand miles, proved of profit, and every incident was entered into with the enthusiasm of a mind which years could not make old. A number of papers upon the Hawaiian volcanoes were the result of this summer's outing, and in the winter of 1889–90, he prepared a volume on Volcanoes, a companion to that on Corals and Coral Islands, a new edition of which was issued at the same time. The prefaces of both works were dated on his seventy-eighth birthday, February 12, 1890.

In the summer of 1889, he attended the meeting of the American Association at Toronto, the first time he had been present at such a meeting since he delivered the presidential address more than thirty years before.

With the autumn of 1890 came a more serious illness than any since 1859, and the indications seemed very alarming. For a number of months absolutely no work was done, and later only a little light labor by means of dictation. It was at this time that the small volume on the New Haven region entitled "The Four Rocks," was given to the public. This disability was again partially thrown off—although he never again resumed active College duty—and the work on the fourth edition of the Manual of Geology, then far advanced, was resumed slowly at first and then with more vigor with returning

* See this Journal, vol. xxxiv, 349, Nov. 1887.

strength. From this time, however, till the end he seldom exceeded a limit of three hours labor each day.

In February, 1893, the printers began their work on the volume mentioned and it was just two years before the last proof had been read and the volume was complete. To himself and still more to those about him it seemed many times as if the completion of this great work would have to be left to others, but with the self-control born of a strong will and long experience, and with the never failing watchful care of his life-long companion—without which his labors could never have been so productive nor have been continued so long—he worked on slowly, doing each day only what he had strength for, and, finally, the labor was accomplished. The completion of this work, which was rewritten and rearranged from beginning to end, involving a critical consideration of the many new facts and theories of the science, will be granted to have been a remarkable performance for a man of eighty-two. He finished it in February, 1895, and a month later he had completed the manuscript of a new edition of his Geological Story and then commenced work on that of the Text Book.

On Saturday, April 13th, he took his usual excursion to the Post Office, and through the day was as bright and vigorous of mind as ever. That evening there was a recurrence of a slight trouble in the action of the heart, of which there had been some manifestations in the few months immediately preceding; the following day he did not rise, although feeling relieved; in the evening the trouble returned and after a very brief period of unconsciousness, he passed quietly away.

The concluding years were marked by an ever increasing serenity, and happiness in his work and in the friends about him. Up to the last day there was no evidence of diminished mental force, though his physical strength was somewhat impaired. It was for him a most happy ending of a life, full of fruitful activity and honor.

The chief scientific results of this long life of continued and, except for its limitations, ever happy labor for science have been already indicated. To estimate properly their value and originality belongs to another place and time and demands the services of specialists in each of the three departments of Mineralogy, Geology and Zoölogy. Some further general words in regard to them seem, however, to be required.

The subject, to which he was earliest attracted, from the time of his first excursions, as a boy, after minerals, and that with which his name is, perhaps, most frequently connected is Mineralogy. The first edition of the System of Mineralogy was issued, as has been stated, in 1837, when he was only twenty-four years old. This large volume shows a close study of the great works of Häuy, Mohs and Naumann and of others who had preceded. It is, however, more than an industrious compilation from earlier authors, particularly as regards the chapters on crystallogeny and mathematical crystallography. The classification adopted is the so-called Natural System, the serious shortcomings of which were later fully appreciated. The nomenclature attempted, devised by him to suit this classification, was on the dual Latin plan "so advantageously pursued in Botany and Zoölogy." The second edition of the System (1844) preserved these features, but in a supplement, a classification based on chemical principles is proposed and this, further developed, is adopted in the third edition (1850) while the Latin nomenclature is abandoned.

In connection with this fundamental change, it seems worth while to quote from the preface of this edition, since what is said here was so characteristic of the author's attitude of mind to scientific truth in general.

> . . . To change is always seeming fickleness. But not to change with the advance of science, is worse; it is persistence in error; and, therefore, notwithstanding the former adoption of what has been called the Natural History system and the pledge to its support given by the author, in supplying it with a Latin nomenclature, the whole system, its classes, orders, genera and Latin names have been rejected. . . .

It was in the fourth edition of the Mineralogy, in 1854, that the chemical classification, essentially as now understood, takes

its full place. In this edition, moreover, the other parts of the work were put in new and better form, containing the result of much thought on crystallogeny and homœomorphism. The fifth edition (1868), which includes only the description of species, is a monumental work—the most complete treatise, indeed, that had ever been attempted. In it the classification was still further developed, the nomenclature simplified and systematized, and in connection with the latter subject an exhaustive review of the entire mineralogical literature from the beginning was made in order to unravel the vexed questions of the history and priority of mineral names. This last feature of the volume was a labor involving great patience and skill. It was in recognition of this work that he received the degree of Doctor of Philosophy from the University of Munich in 1870. In the sixth edition of the System (1892), by his son, he took a lively interest, but was unable to coöperate in the labor actively, in consequence of the condition of his health; even the reading of the final proofs, though attempted, had to be soon given up.

Besides the System, he also issued a small work, called the Manual of Mineralogy, which has passed through four editions (1848, 1857, 1878, 1887). The pages of this Journal also contain, particularly down to 1868, many papers on mineralogical topics; his last paper in this field was published in 1874. The subjects that interested him were, for the most part, those of a general and philosophical nature, such as questions of classification, theories of crystallogeny, and the morphological relations of species. In the points connected with the descriptions of individual species he took less interest, though his observations here were numerous and important.

Mineralogy, however, did not afford scope enough for a mind so active, indeed he often spoke of it as a department of limited ideas and principles. To the broader field of Geology and geological investigation, he had been early turned by his labors for the Exploring Expedition, the results of which have been already mentioned.

The several editions of the Manual of Geology (1862, 1874, 1880, 1895) have been briefly alluded to. To the many geologists familiar with this work, it is unnecessary to remark that, like the System of Mineralogy, it is not simply a compilation

of the facts of the science but a development of the whole subject with a breadth, philosophy and originality of treatment that has seldom been attempted. One of his colleagues remarks:

"The treatment of strata and fossils from a chronological point of view as Historical Geology is a characteristic feature of his Manual. The growth and development of the earth, its continents and seas and the progress in the organic life on its surface, were thus unified into a special department of Geology, the history of the earth and of its inhabitants, which was by other authors dealt with as formational, stratigraphic or paleontologic geology."

Each edition of the Geology was carefully worked over and the last was completely rewritten from beginning to end. It was a great pleasure to him in connection with this work to have the constant and ready coöperation of a number of the able young geologists in the country, without whose aid the volume could not have been so satisfactorily completed. Similar coöperation and pleasant relations he had enjoyed while at work upon his earlier volumes both in Geology and Mineralogy, but this is hardly the place to speak of that in detail. Allusion has also been made to the smaller works, the Text Book (first edition, 1864,) and the Geological Story (1875); of the last the manuscript of a new edition is now in the printers' hands.

In the general department of Geology his contributions again were largely to subjects of a broad and philosophical character: the origin of continents and of the grand features of the earth was discussed in early papers as well as later; the problems of mountain-making and the phenomena of volcanic action, to which he devoted much thought, are some of the other topics treated at length.

But, as a geologist, he was not only a thinker and writer in his study but also an active observer in the field. This remark applies obviously to the four years with the Exploring Expedition but further particularly to the period from 1872 to 1887, when he was carrying on the study of the crystalline rocks of the so-called Taconic system chiefly in western New England; also of the glacial phenomena of southern New England (1870 *et seq.*) The region included in western Connec-

ticut and Massachusetts, and extending westward into New York and north to Vermont, was tramped and driven over many times, until one might almost say that there was hardly an outcrop accessible to any of the roads in this difficult region that had not been visited, its rocks examined and observations recorded on the dip and strike. These results and the conclusions derived from them fill many pages of this Journal. Against the dictum that all crystalline rocks, not volcanic, must be of pre-Paleozoic age, he rebelled strongly as against all similar dogmatic treatment of scientific facts and principles. His strength of feeling on this point was what largely prompted him to spend so much time and strength in this investigation.

He was no less interested in the country immediately about New Haven, especially as regards its glacial phenomena. In 1870, he published a large memoir on the Geology of the New Haven region. The observations, recorded in this paper, were made at a time when work at his table was impossible and the open-air exercise brought profit to health as well as scientific results. Twenty years later, when again incapacitated from writing and close thinking, he issued a small volume entitled "The Four Rocks of the New Haven region" describing some of the chief features of the region in popular form.

Thus far only his labors in Mineralogy and Geology have been spoken of in particular, and probably most of the younger generation of workers in science know him only in these fields. But his most extensive original contributions to science were in the department of Zoölogy, to which he made early contributions although chiefly attracted to it by the chance opening when on the Wilkes Expedition. The large volume devoted to the Zoöphytes, and the two volumes of the Crustacea, each work with an atlas of beautiful plates most of them drawn by himself, are classical works containing the descriptions of hundreds* of new species and with a philosophical development of the classification and the relations of species that is truly

* The number of new species of zoophytes described was over two hundred; in the Report on Crustacea six hundred and eighty species were described, of which upwards of five hundred were new. A large part of the collections in Crustacea were lost by the wreck of the Peacock on the shores of Oregon. It may, perhaps, be worth recalling that many of the type specimens were later de-

profound. It is in this matter of the classification that the most important contribution to Zoölogy was made. This is true in general of both the works, and though the last half century that has elapsed has brought some slight changes to the classification of the Crustacea here developed, that of the Corals stands to-day nearly as it was given in the Expedition Report.

The volume upon the Zoöphytes is what would be called to-day a report on the Anthozoa, including the description of the corals and coral-making animals and of allied forms, of sea-anemones and including also a few hydroids. The value of the work is much increased by the fact that it was the first time that any considerable number of the coral animals had been described and figured from life; the original colored drawings were made by Mr. Dana from the living animals, as described in the quotation below, taken from the preface. The beautiful drawings of the sea-anemones, it should be stated, were made by the artist of the Expedition, Mr. Drayton. The volume thus marked a new era in the subject, since collections had hitherto been limited for the most part to the corals themselves.

. . . . . The field for geological investigation there offered [the Fiji islands], was limited, as we were shut out from the interior of the islands by the character of the natives: at the same time coral reefs spread out an inviting field for observation, hundreds of square miles in extent. The three months, therefore, of our stay in that group were principally devoted to exploring the groves of the ocean, where flowers bloomed no less beautiful than those of the forbidden lands, and rocks of coral growth afforded instruction of deep interest. The specimens were obtained by wading over the reefs at low tide, with one or more buckets at hand to receive the gathered clumps, or where too deep for this, by floating slowly along in a canoe with two or three natives, and through the clear waters, pointing out any desired coral to one of them, who would glide to the bottom, and soon return with his hands loaded, lay down his treasures, and prepare for another descent. When taken

stroyed by fire in Chicago, while the copies of the published work suffered three times most seriously in the same way. The first time was during its publication at Philadelphia and resulted in the loss of many of the original colored drawings, to the permanent injury of the work, since they could not be replaced. The two other fires were at New Haven, the last one (1894) largely destroyed the residue of the plates when being collated by the binder preparatory to their being presented to some friends of the author.

out of its element, the coral often appears as if lifeless: but placing it in a basin of sea-water, the polyps after a while expand, and cover the branches like flowers. Four-fifths of the observations in this department were made at the Feejee Group. . . . . .

The work accomplished on the expedition is the more remarkable, because there was from the first but little sympathy between the prominent naval officers and the active members of the scientific corps. This lack of coöperation resulted in the throwing of many obstacles—sometimes petty and provoking, again very serious—in the way of the young and ardent observer, and it is only fair to him to allude to this subject here, though it was one of which he was by no means fond of speaking. There is a painful contrast between the course of events in these particulars with the Wilkes expedition and the cordial aid given to science in some of the later ones.

Many papers upon zoölogical subjects were published in this and other Journals, especially during the time he was working up the collections of the Exploring Expedition, and these present many of the results and conclusions arrived at. The principle of Cephalization, or the domination of the brain in determining the development of an animal organism, was first brought out in 1852.* In regard to this subject, particularly in its relation to evolution, he says in the Manual of Geology (1895, p. 439):

This subject has much interest in connection with the successional lines in the animal life of the globe which geology has brought to light. But the preceding remarks are not to be understood as intimating anything with regard to the origin of species. There was no such reference in the author's first presentation of the views in 1852. At that time the idea of evolution by natural causes had scarcely an advocate; for Darwin's work did not appear until 1859. Neither are the facts now to be regarded as adding to the causes of derivation. This much, however, may be learned from them:—

1. Whatever the natural causes or methods concerned in evolution, organic conditions have determined lines, limits, and parallel relations, in accordance with the principle of cephalization.

* In the Report on Crustacea; in 1863 the subject was discussed in this Journal.

2. In the evolution of the animal kingdom a "tendency upward" is a necessary consequence of the presence of a cephalic nervous ganglion or brain.

The theory of evolution, or the development of species, was one, as indicated above, that his mind approached slowly. He started, like most others, with the belief in the special creation of species; at the same time, his mind even at this period was opening out to a broader idea of the relation of species to each other. This is hinted at in the closing sentences of the following paragraphs quoted from a chapter on the geographical distribution of Crustacea.*

. . . . . Although we cannot admit that circumstances and physical forces have ever created a species (as like can only beget like and physical force must result simply in physical force) and while we see in all nature the free act of the Divine Being, we may still believe the connexion between the calling into existence of a species and the physical circumstances surrounding it to be as intimate nearly as cause and effect."

In 1857 again, in a paper upon Species, published in this Journal (vol. xxiv), he says, (p. 307, the italics are his):

A species among living beings, then, as well as inorganic, is based on *a specific amount or condition of concentered force defined in the act or law of creation.*

On a later page, he again speaks of a species as "essentially permanent or indestructible."

He always maintained, however, that the true scientific spirit was to keep the mind open to the reception of new truth, even if this was at first opposed to preconceived notions. This principle he had exemplified in regard to a subject of limited bearings by the change of view on mineralogical classification, as is well shown by the quotation from the preface to his Mineralogy given on a preceding page. And now in relation to this, perhaps the broadest generalization in science, he was true to this principle again. For gradually, by steps that it would be interesting to trace, he came to accept very fully the principle of evolution as a fundamental law,

* Report on Crustacea; also this Journal, vol. xx, 358, 1854.

although it should be said that Darwinism in the narrow sense never seemed to him a sufficient explanation of the origin of species. To attempt to explain his views in full would be inappropriate in this place, but by quoting a few sentences from the closing chapter of the last edition of his Manual (1895), the main points in the position finally reached may be shown.

. . . . The principles above stated are all in accord with a theory of evolution and through the added facts of later years, they favor the view of *evolution by natural variation.*

. . . . It is perceived that the law of nature here exemplified is *not* "like produces like," but like *with an increment* or some addition to the variation. Consequently, the law of nature, as regards kingdoms of life, is not permanence but change, evolution. . . . . The survival of the fittest is a fact; and the fact accounts in part for the *geographical distribution* of the races of men now existing and still in progress; but not for the *existence* of the fittest, or for the power that has determined survival. . . . . But the origin of the variation is without explanation. And so it is for the most part throughout the kingdoms of life. Enough is known to encourage study.

And finally, the closing paragraph of the work is as follows:

Whatever the results of further search, we may feel assured, in accord with Wallace, who shares with Darwin in the authorship of the theory of Natural Selection, that, the intervention of a Power above Nature was at the basis of man's development. Believing that nature exists through the will and ever-acting power of the Divine Being, and that all its great truths, its beauties, its harmonies, are manifestations of His wisdom and power, or, in the words nearly of Wallace, that the whole Universe is not merely dependent on, but actually is, the Will of one Supreme Intelligence, Nature, with man as its culminant species, is no longer a mystery.

These are the words of the Christian Philosopher, with a rarely comprehensive grasp, and with whom the faith of his youth only grew stronger as his insight became deeper into Nature's laws.

As an editor of this Journal, Professor Dana was associated first with the two Sillimans (1846 to 1863), later with Benjamin Silliman, Jr. alone (1863 to 1875) and finally with his son Edward Salisbury, from 1875. The elder Silliman died in 1864 and the younger Silliman in 1885. The editorial labors were carried on almost continuously from 1850 to the end of his life. Ill health interrupted this work less than that involving severer and more consecutive thought. The closing pages of the present number contain several notices prepared by him within the past few weeks.

In connection with this labor, he did a vast amount of writing, including, besides original papers, hundreds of abstracts, critical reviews, obituary notices, and notes on many topics. These are far too numerous to find place in the Bibliography here given. He threw into this editorial work much of his best energy and always felt that he was serving science well in this way. No degree of pains was too great to ensure completeness and accuracy, and if an outsider might have thought that he insisted too strongly upon some rule of punctuation or spelling, it would have been from the failure to understand a mind which could be satisfied only with the highest degree of accuracy and excellence attainable. A piece of manuscript written for the Journal, like that of his books, was corrected and amended again and again, and the process of erasure and insertion of new words and paragraphs went on up to the moment of its passing into the printers' hands; the result was often trying to the compositor notwithstanding the clearness of the hand-writing.

As a College Instructor his labors commenced in 1855 and, except as interrupted by ill health, as has been explained, continued until 1890; in 1892 he formally retired and, in 1894, was made *Professor Emeritus*. He gave instruction at first in Mineralogy and Geology, but afterward in Geology alone, with occasional courses of lectures, as on Evolution and Cosmogony. The subject of Geology did not occupy a large place in the curriculum and consequently the number of exercises per week was not large. This, as he appreciated fully, was a great gain to him personally, so far as original writing was concerned, for it not only gave him much of his time for his own work but

during seasons of ill health made the strain as light as possible. It had the accompanying disadvantage, however, that it did not bring him so near to the successive classes of young men as would otherwise have been the case. His personality, however, was so strong, his interest in the subject he was teaching so profound, his patience in explanation so untiring, that few of his many pupils could have failed to carry away a lasting impression of him, if not always of his subject. His relations with the students, always friendly, were made more close by the excursions to the various points of interest about New Haven and its vicinity, which he enjoyed himself quite as much as the boys and in much the same youthful spirit. These excursions were generally largely attended, and by many whose tastes did not lead to science; not a few of them will remember the earnest manner of the genial Professor in his out-door lectures and the quick step with which he led them up and down the hills, faster perhaps, in some cases, then they would have chosen to go.

In the deliberations of the College Faculty, he was always in favor of progress and especially interested in any step leading to the development of science. He was active in the building up of the University collections in Mineralogy and Geology, not only in the early years but also later as a Trustee of the fund given to the University by Mr. George Peabody in 1866 for a Museum of Natural History. The construction of the building erected in 1876, as regards internal arrangements, was largely determined by plans made by him. He also coöperated cordially in the establishment of the Scientific department of Yale University, known as the Sheffield Scientific School, and always took a sincere pleasure in its progress. The profound results of his influence, particularly in encouraging his younger scientific colleagues, can hardly be overestimated.

Of his habits of work, the constant activity of his mind, and of many personal characteristics, aside from those already hinted at, much might be said; but of these points it is more appropriate that others than the writer should speak, as also of the wonderful powers of generalization of one, who was a master of three sciences and at the same time had a profoundly comprehensive view of nature as a whole. Of his unquestioning religious faith, too, this is not the place to speak

Of the honors which fall to the successful worker in science, Professor Dana received a large number, but his mind was too free from pride or ostentation to dwell upon them. It would be most in accordance with his habit to omit any detailed statement here, but this account would then lack completeness.

In 1872 the Geological Society of London conferred on him the Wollaston medal, "in acknowledgement of his services to Mineralogy and Geology." In 1877 he received the Copley gold medal from the Royal Society of London, "for his Biological, Geological and Mineralogical investigations, carried on through half a century, and for the valuable works in which his conclusions and discoveries have been published." In 1892 the Boston Society of Natural History conferred upon him their "Grand Walker prize of $1000 for distinguished services in Natural History."

Professor Dana was elected president of the American Association for the Advancement of Science in 1854 and in August of the following year delivered his retiring address at the Providence meeting. In 1872 on the celebration of the fourth centennial of the University of Munich, he received the degree of Ph.D. and in 1886 at the Harvard celebration the degree of LL.D., was conferred upon him. The latter degree had been earlier given by Amherst College in 1853 and was also received from the University of Edinburgh in 1886. He was one of the original members of the National Academy of Sciences in the United States, and since the time when he was made correspondent of the Academy of Natural Sciences in Philadelphia in 1836, such honors were frequently conferred upon him, until he became thus connected with a large number of the scientific societies in the United States and abroad, including the Royal Society of London, the Institute of France, the Royal Academies of Berlin, Vienna and St. Petersburg and many others.

Professor Dana leaves a widow, four children, and four grandchildren.

The photograph from which the accompanying plate was made was taken about six weeks before his death.

E. S. D.

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THE

AMERICAN JOURNAL OF SCIENCE

[THIRD SERIES.]

ART. XXVIII.—*On the Color Relations of Atoms, Ions and Molecules;* by M. CAREY LEA. Part I. (With Plate IV.)

THE atoms of which elements are composed differ remarkably in color from the elements themselves; their colors are more important and more characteristic than those of the elements, and if we divide the entire series of elements into two classes, those whose atoms are always colorless whatever may be their valency, and those whose atoms are either sometimes or always colored, we shall find that this division harmonizes in a striking way with their chemical properties. The colors of the elements have no such significance or importance.

This present paper accepts the Arrhenius theory of dissociation, the author believing that the evidence in its favor is too strong to be resisted. But the facts to be stated, and the conclusions to be drawn therefrom are independent of any theory.

It is somewhat remarkable that it is never possible to deduce the color of an atom from that of the element which it forms by combining with another similar atom. Between the two, the atom and the element, there seems to be no color relation whatever. It is from the combinations of an atom with one or more dissimilar atoms, kathions with anions, that we can with facility and certainty deduce the color of the atoms themselves.

So far I have spoken of atoms only, but the matter in hand is simplified by considering dissociated ions also. And as a first step it becomes necessary to establish the following proposition: namely, that in any colored inorganic compound in solution, the color belongs essentially to the metallic atom, whether it exists in a free state as an ion or combined with a

dissimilar atom or atoms to form a molecule. That is to say it does not belong to the ion with exclusion of the molecule as some have held, nor to the molecule with exclusion of the ion as has been held by others. Color when it appears, is the essential property of the atom, possessed by it in the free state and carried by it into any electrolyte which it forms.

This fact can be conclusively proved from the researches of Glan and of Ewan. Each of these chemists studied the action of copper salts and more particularly of the sulphate. Both observers used virtually the same method. A ray of light was passed through a small stratum of strong solution and then through a larger quantity of distilled water and the amount of absorption was noted. In another parallel tube the two were mixed and the amount of absorption was compared, in each case for particular wave lengths. Ewan used an eight-fold dilution. Glan usually a seven-fold but sometimes a three or five. In all cases the difference found was extremely small, scarcely if at all exceeding the magnitude of experimental error.* Had the color been a property of the ion only, or of the molecule only, the differences found would have been very great, in opposite directions.

Ewan calculates from the numbers found by Kohlrausch that in a solution of cupric sulphate containing 2·38 gram equivalents to the liter, the dissociation amounts to 15·3 per cent. A dilution reducing the proportion to 0·2856 equivalents to the liter increases the dissociation to 31·7 per cent. Therefore, if the color depended upon the ions only, the total absorption would be more than doubled. On the other hand if the color depended upon the molecules only, the absorption would be materially diminished. Now the work of Ewan, of Glan, and of previous observers shows that neither of these large changes takes place but that the absorption varies between narrow limits. Therefore it is certain that the color belongs to the atom, whether it exists as an ion or whether by union with a dissimilar ion, it forms part of an electrolyte.

These proofs would seem to be sufficient but others can be had in abundance. In dilute solutions of cobaltous salts the ions exhibit the color characteristic of cobalt. But cobalt cyanide also exhibits that color; it is quite anhydrous, no ions can be present and therefore the color must be due to the atoms. Cobalt carbonate exists in two forms, one freely hydrated, the other anhydrous, both show the characteristic color. In the hydrated salt the ions may possibly be dissociated, in the other they cannot be. Nickel cyanide is also anhydrous and yet shows the characteristic nickel color.

* Both Ewan's and Glan's results will be found tabulated in Dr. Ewan's paper in the Philosophical Magazine, vol. xxxiii at p. 336. (1892.)

Chromic chloride after sublimation still shows the characteristic pale violet color of chromic salts.

These instances might be multiplied but they will sufficiently show that characteristic color belongs to the atom as well as to the ion.

When the atom enters into a molecule such as is produced by the union of an elementary kathion with an elementary anion, of course that molecule will not give exactly the same absorbtion spectrum as the free ion: the vibration of the ion is free whereas that of the atom in the molecule is constrained. What is contended for is that in the great majority of cases the color of the ion and that of the atom are substantially the same. Exceptional cases will occur, difficult to explain under any theory. Chromous chloride gives a blue solution in water, chromous acetate a red one: can therefore the chromous ion be both red and blue?

This case is quite the reverse of the results obtained by Ostwald in his well-known work done on the permanganates.

The green solution when concentrated of copper chloride is a case often cited to show that green molecules may yield blue ions. But this may be explained in quite a different way. It is known that many salts exist in strong solutions, as complex molecules. Hittorf has shown that cadmium iodide in strong solution in water exists as $(Cd\ I_2)_2$. Lenz* gives as a formula for the solution of potassium iodide in alcohol

$$a(KI),\ b(KI)_2,\ c(KI)_3,\ \text{etc.}$$

the coefficients a, b, c diminishing rapidly.

It is quite probable that the green color of some copper compounds may be due to complex molecules and among them, copper chloride.

Criteria of Color.

In making determinations of the colors of ions, and therefore of atoms, I have used the following criteria.

1. When an electrolyte gives a solution in water which is colorless when dilute, both the kathion and the anion are colorless. Thus for example as lithium bromide gives a colorless solution in water it follows that the ions of lithium and bromine are colorless. It has been already said that no relation whatever exists between the color of an atom and that of its molecule. So two colorless bromine atoms form the intensely colored element bromine. If further proof be required of the colorless nature of the bromine atom it is easily obtained by considering that the compounds formed by that atom with

* Mem. de l'Ac. Imp. de St. Petersburg, 30.

all the alkaline and earthy metals are colorless even when not dissociated. As potassium iodide forms a colorless solution in water it follows that the atoms of both potassium and iodine are colorless. Sodium monosulphide gives a colorless solution in water, therefore the atoms of sodium and of sulphur are colorless. But the polysulphides are yellow in solution: it follows therefore that in them a certain portion of the sulphur may exist in a molecular condition.

2. If an electrolyte gives a colored dilute solution in water it is necessary first to consider the constitution of the anion. If this is a single atom, then the color of the solution belongs entirely to the kathion. For it is a very remarkable fact that all elementary anions are colorless. This is all the more curious that the endless number or organic coloring matters are built up chiefly of these colorless anions and of colorless hydrogen.

This criterion enables us to judge as to a large number of atoms. As oxides, fluorides, chlorides bromides, etc, all have colorless anions, whatever color is shown by their *dilute solutions* must be due to the kathions.

3. Even if the anion is composite, information can often be gained. Many composite anions are colorless, for example So_4. So that when sulphates give solutions that are colored when dilute the color must be due to the kathion.

The same is the case with nitrates, phosphates, carbonates, etc. In these cases and in many others, knowing the anion to be colorless we are certain that the kathion must contribute any color that is present.

These criteria will afford the means of deciding upon the color of the entire series of elementary atoms.

Classification.

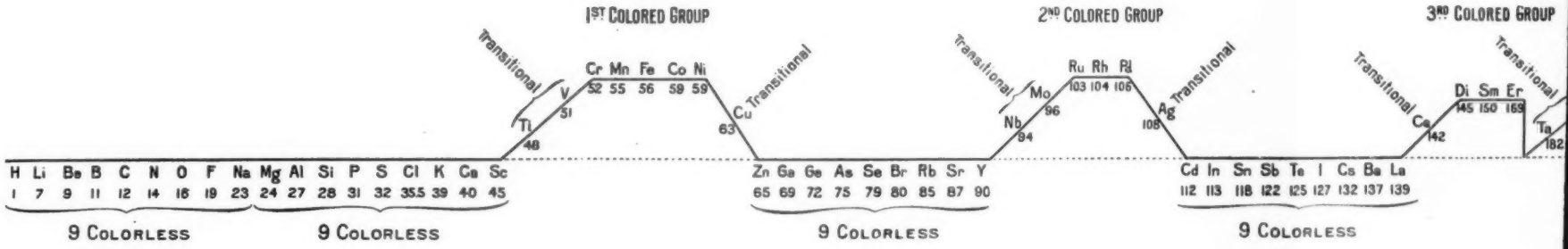
In the preceding sections proof has been offered that the colors of the atoms are substantially the same as those of the corresponding ions. Especially the fact that a solution of copper sulphate by a dilution which doubles the number of its dissociated ions scarcely shows the slightest change of total absorption is strong, one might say, final.

But as respects classification which will form the chief subject of the present paper it is absolutely unimportant whether these views be accepted or not. We may classify the elements according to the color and want of color of their ions or quite

Am. Jour. Sci., Vol. XLIX, 1895.

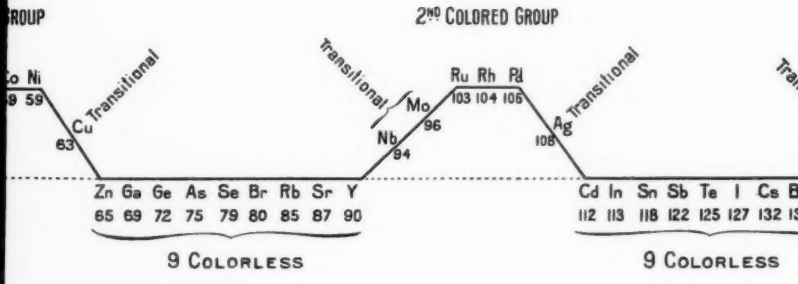
PERIODIC LAW OF COLOR

COMPRISING ALL THE ELEMENTS IN NUMERICAL ORDER



RIODIC LAW OF COLOR

ALL THE ELEMENTS IN NUMERICAL O



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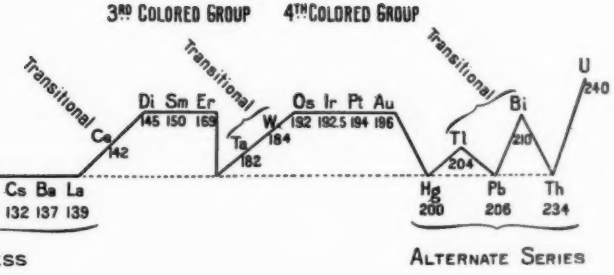
3RD COLORED GROUP
4TH COLORED GROUP
Transitional
Transitional
Transitional
Cs Ba La
132 137 139
Ce
142
Di Sm Er
145 150 165
Ta
182
W
184
Os Ir Pt Au
192 192.5 194 196
Hg
200
Tl
204
Bi
210
Pb
206
U
240
Th
234
ALTERNATE SERIES

indifferently, by that of their atoms: the result will be identical.

The color of the atom is always easily ascertained and could be even if the dissociation theory had never been suggested.

The color of the atom has nothing to do with the element, for it we must go to the salts.

Finding that the chlorides, bromides and iodides of the alkaline metals and of calcium strontium, etc., are all colorless even in the solid form, we conclude that all the atoms in question are colorless since colored constituents do not form colorless compounds. When a metal combining with a colorless acid forms a colored compound we know that the atom of the metal is colored. We do not need to inquire for present purposes what that color is, all that we need to determine is whether color is present or not. In fact this matter is so simple that the color or absence of color of the atoms and the conclusions to be drawn therefrom might have been deduced generations ago from facts already then familiar.

From this we can obtain the results sought which are, first, a new classification of the elements based on more correct principles than those previously made, and second, a proof that *the color or non-color of an element is a function of its atomic weight.*

Elementary Ions.

Considering the elements in numerical series, we find:

1. Elements with atomic weights not exceeding 47 have colorless ions only.

2. With titanium (48) colored ions suddenly commence and we at once have a series of eight unbroken, viz: Ti (48), V (51·2), Cr (52·4), Mn (54·8), Fe (56), Co (58·6), Ni (58·6), Cu (63·4).

3. Next follows a series of nine metals with colorless ions only: Zn (64·9), Ga (69·9), Ge (72), As (74·9), Se (78·9), Br (79·8), Rb (85·2), Sr (87·2), Yttrium 92·5.

4. Then six metals with colored ions: Nb (94), Mo (95·8), Ru (103·5), Rh (104·1), Pd (probably,) (106·2), Ag (107·7).

5. Then nine more metals with colorless ions: Cd (111·6), In (113·4), Sn (117·8), Sb (122), Te (125), I (126·5), Cs (132), Ba (136·8), La (139).

6. Then ten more with colored ions: Ce (142), Di (145?), Sm (150), Er (169), perhaps Ta (182), W (184), Os (192?), Ir (192·5), Pt (194), Au (196·2).

7. Up to gold, the colored and colorless ions present themselves in large blocks of each kind. But the six remaining metals are of each sort alternately, thus Hg (199·8) colorless; Tl (203·6) colored; Pb (206·4) colorless; Bi (210) colored; Th (234?) colorless and finally U (240) colored.

Eleven metals have both one or more colored and one or more colorless ions.* For the moment these have been classed together with those that have colored ions only, in order to divide the entire series into two great classes.

The distinction however between so-called elements having none but colored ions and those having both colored and colorless is of very great importance and will be fully considered further on.

Placing the foregoing in tabular form we have :—

Ions colorless, 18	H 1	Ions colored, 8	Ti 48
	Li 7		V 51·2
	Be 9·3		Cr 52·4
	B 11		Mn 54·8
	C 12		Fe 56
	N 14		Co 58·6
	O 16		Ni 58·6
	F 19·1		Cu 63·3
	Na 23		
	Mg 24·3	Ions colorless, 9	Zn 64·9
	Al 27·3		Ga 69·9
	Si 28		Ge 72
	P 31		As 74·9
	S 32		Se 78·9
	Cl 35·5		Br 79·8
	K 39		Rb 85·2
	Ca 40		Sr 87·2
	Sc 45		Y 92·4
Ions colored, 6	Nb 94	Ions colored, 10	Ce 142
	Mo 95·8		Di 145
	Ru 103·5		Sm 150
	Rh 104·1		Er 169
	Pd 106·2		Ta ? 182
	Ag 107·7		W 184
			Os 192
Ions colorless, 9	Cd 111·6		Ir 192·5
	In 113·4		Pt 174
	Sn 117·8		Au 196·2
	Sb 122		
	Te 125	*Alternate.*	
	I 126·5	Colorless Hg	199·8
	Cs 132	Colored Tl	203·6
	Ba 136·8	Colorless Pb	206·4
	La 139	Colored Bi	210
		Colorless Th	233·9 ?
		Colored U	240

* This expression is used for brevity and with the intention of expressing the fact that an elementary ion may assume different colors with different valencies.

The Law of Color.

In the first part of this paper has been developed the conception that the color of the atom is all-important whilst that of the element has little significance. That there exists no relation whatever between the two, so that the color of the atom can never be deduced from that of the element. But the color of the ion can always be found by certain criteria which have been given and it has been shown that the color of the atom is the same as that of the ion. Both may or may not change with changes of valency.

Several interesting results follow from this conception. It appears that we must reject the well-known Periodic Law as being based on erroneous principles.

Another result is the establishment of the Law of Color, which may be formulated as follows:

No element having ions colored at all valencies can belong to the same natural group with elements having colorless ions only.

This law is rigorous and fundamental: rigorous because it admits of no exception; fundamental because it divides elements into two chief divisions with strongly marked differences.

They even differ in the method of classification which they require. The colorless elements fall into groups with atomic weights widely differing, the elements with colored ions tend to fall into series with atomic weights immediately following each other.

The periodic Law which we owe to Newlands, Mendeléef and Lothair Meyer, beautiful and fruitful as it has proved, contains nevertheless defects of a serious character; some already recognized, and condoned only in view of its great merits and services.

For the three metals copper, silver and gold the periodic law affords absolutely no place. The numbers of their atomic weights made it necessary to insert them amongst the metals of the alkalies, where they are thoroughly out of place. The fact that there was no choice but to put them there is in itself a proof that the law of octaves rests on a false basis.

A very grave fault is the complete exclusion of hydrogen. A system must be defective which finds a place for one element of water and none for the other, and which totally excludes the most important of all the kathions. This exclusion is so complete that in the published tables of the periodic law the symbol for hydrogen does not generally appear.*

* Cf. Modernen Theorien, pp. 140, 143. Ostwald, Lehrbuch 2d German edition pp. 134, 135. Ramsay's Chem. pp. 628, 629.

This exclusion cannot be explained or accounted for in any way. Hydrogen simply will not fit in to a proper place, but has to be excluded to obtain symmetry.

Then there are the three metals, iron, cobalt and nickel and the six platinum metals. For all of these there is no place, and one has to be forcibly made. Whether this is accomplished by making them a fragmentary and disjointed eighth column as done by Lothair Meyer or whether they are inserted, three of them into each of a second, third and fifth vertical column, as done by Mendeléef, the effect is in either case forced and unnatural. These elements cannot like hydrogen be simply excluded, they must be placed somewhere, but one feels the symmetry is destroyed. Another most serious objection is to the exclusion of sodium from the series of the alkaline metals.

In both tables chromium and molybdenum are placed in the oxygen group and in Mendeléef's, fluorine and manganese constitute a group. All the metals having ions colored at all valencies are out of place. Other faults might be cited but the above are sufficient to show that the periodic law is a singular mixture of truth and error.

Periodic Systems.

The body of the elements separates itself as we have seen into two great divisions those with ions always colorless and those with ions always colored.

These two classes are always distinct and the elements forming each have no relation with the other ; that is to say, we shall never find in natural groups elements belonging to more than one of these two great divisions. The remarkable manner in which they meet at particular points or nodes and melt into each other will be described farther on. At present we have only to do with the consideration of classes taken separately.

First Division. Ions all Colorless.

And first as to the colorless class. If we arrange all its members in numerical order so as to form vertical columns of nine each, then if we read the horizontal lines we shall find that *the entire class of elements with colorless ions is divided*

TABLE I.—FIRST DIVISION OF ELEMENTS.

Elements with all Colorless Ions in numerical order, forming nine Natural Groups.

Valency.						
I	H 1	F 19	Cl 35·5	Br 80	I 127	.....
	Li 7	Na 23	K 39	Rb 85	Cs 132	.....
II	.....	.....	Ca 40	Sr 87	Ba 137	.....
III	.....	.....	Sc 45	Y 90	La 139	.....
II	Be 9	Mg 24	Zn 65	Cd 112	Hg 200	.....
III	B 11	Al 27	Ga 69	In 113	.....	.....
IV	C 12	Si 28	Ge 72	Sn 118	Pb 206	Th 234
V	N 14	P 31	As 75	Sb 122	.....	.....
VI	O 16	S 32	Se 79	Te 125	.....	.....

into nine great groups, all absolutely natural, each element in its proper place accurately fitted.

An examination of Table I will show,

1. Hydrogen stands at the head of the halogen group, with the members of which it makes countless substitutions. Hydrogen has always been an element difficult to class, but this is its proper place.*

2. Next follows the group of the metals of the alkalies, with sodium in its right place. With these, hydrogen is intimately connected.

3. The calcium group begins with that metal, either because earlier members with lower atomic weights exist, but have not been discovered, or because the group naturally commences at a later stage than the preceding. The same thing is true with the scandium group next following.

4. The remaining groups need no particular description. They are eminently natural and very familiar.

5. In these groups following the horizontal lines, all members of each group have the same valency. To this there is no exception.

The foregoing applies to this table considered as groups corresponding to the horizontal lines. When it is intended to consider the serial relations according to columns they should be taken as one long serial without breaks.

Much importance has naturally been attached by Mendeléef to the progressive stages of oxidation in his groups, as for example, the series

$$Na_2O,\ Mg_2O_2,\ Al_2O_3,\ Si_2O_4,\ P_2O_5,\ S_2O_6,\ Cl_2O_7.$$

And the corresponding hydroxides, hydrides, methides, etc. Of these it may be said that Cl_2O_7 is purely hypothetical. The rest of this series will be found in precisely the same order in the second column in Table I and all the corresponding elements in each horizontal line have the same valencies and tend to form similar compounds.

This table representing the first great division of elements includes all those whose ions function as anions with part of the kathions.

* By Roscoe & Schorlemmer and in the Graham Otto treatise it is placed immediately before the halogens. By Ramsay at the head of the lithium sodium group.

Transitional Elements.

Intermediate between the two divisions is a small class of eleven transitionals. These elements have ions which at some valencies are colored and others colorless.

Transitional Elements.						
Ti 48	*Cu 63·3*	*Nb 94*	*Ag 108*	*Ce 142?*	*Ta 182*	*Tl 204*
V 51		*Mo 96*			*W 184*	*Bi 210*

(As to tantalum and niobium, satisfactory information is deficient and they are placed here provisionally.)

An inspection of the table will show that the metals composing it have little relation with one another.

Most of them on the contrary are noticeable as having each some marked peculiarity. Titanium when heated combines with atmospheric nitrogen. Vanadium forms a compound radical simulating a metal so completely that all chemists were deceived until Roscoe detected the fact. Copper forms a solution which has the property of dissolving cellulose. Silver can assume a condition in which it is freely soluble in water; it is also remarkable for the high sensitiveness to light of some of its compounds. Tungsten is remarkable amongst inorganic substances for the unexampled complexity of its compounds, as first observed by Gibbs. Thallium is noted for uniting in a singular way the properties of an alkaline and those of a heavy metal.

The relations of this peculiar group are chiefly with the elements having colorless atoms only, as shown in Table II. Into this, they enter as it were in a block, at the center, increasing the number of groups to thirteen, or twelve if we take the first two as constituting a double group of univalent elements. In this way as we follow the groups downwards the valency increases successively from one to six, then begins at one again and increases regularly from one to six again. This will be better seen by referring to Table II. In every group each member has the same valency.

Whether it is probable that all the blanks represent so many elements remaining to be discovered seems doubtful. But it is certainly the opinion of many chemists that the number of existing elements as yet unknown, is large.*

* Cf. Ramsay, Inorganic Chemistry, p. 87.

TABLE II.—*Elements with all Ions Colorless, and Transitional Elements (in italics) in numerical order, forming thirteen Natural Groups.*

Valency.						
I	H 1	F 19	Cl 35·5	Br 80	I 127	------
	Li 7	Na 23	K 39	Rb 85	Cs 132	------
II	------	------	Ca 40	Sr 87	Ba 137	------
III	------	------	Sc 45	Y 90	La 139	------
IV	------	------	*Ti 48*	------	*Ce 142*	------
V	------	------	*V 51*	*Nb 94*	*Ta 189*	------
VI	------	------	------	*Mo 96*	*W 184*	------
I	------	------	*Cu 63*	*Ag 108*	------	------
II	Be 9	Mg 24	Zn 65	Cd 112	Hg 200	------
III	B 11	Al 27	Ga 69	In 113	*Tl 204*	------
IV	C 12	Si 28	Ge 72	Sn 118	Pb 206	Th 234
V	N 14	P 31	As 75	Sb 122	*Bi 208*	------
VI	O 16	S 32	Se 79	Te 125	------	------

With elements having atoms always colored the relations of the transitionals are so slight that I hesitated about giving them a place in Table III and have done so chiefly to give emphasis to this fact, that in the entire series of elements *there is not a single case in which an element having atoms always colorless appears in the regular numerical series between a transitional element and one with atoms always colored. Also that there is not a single case in which an element with atoms always colored appears in the numerical series between a transitional element and one having colorless atoms only.*

This will be seen better by examining the diagram embracing the entire series. This perfect regularity seems to justify this new method of classification.

This group contains elements whose atoms function as kathions only.

Second Division. Ions all colored.

In Table III will be found the series of elements with all colored ions and to these have been added the transitionals, distinguished by being printed in italics. The transitionals fit equally well into either of the two great divisions, that of the colorless and that of the all colored ions, with this difference that in the first division they fit into the center, in the second division they act as outliers to the respective series, connecting the colored with the colorless. This last function is however better shown by the diagram at the end. Their chemical relations are with the first division.

The colorless elements when arranged in vertical columns form groups according to the horizontal lines. Members of each group though closely connected in properties, differ widely in atomic weights.

With the elements having all colored ions the case is very different. They fall into four series, members of which have their atomic weights immediately following each other in unbroken succession.

The first of these series consists of the metals chromium 52, manganese 55, iron 58, cobalt 59, and nickel 59. This is a very well marked group, the chromates, manganeses and ferrates being isomorphous. Also the sesquisulphates of the three metals replacing each other in the alums.

Chromium and manganese were formerly always placed in the iron group until the exigencies of the Periodic Law required the transfer of chromium to the oxygen group and of manganese to the univalent halogen group, a translocation for which there seems no sufficient justification.

TABLE III.—SECOND DIVISION.

Elements with Ions always colored. Also Transitional Elements (in italics) in Numerical Order.

Trans.	Ions always colored.	Transitional.		Ions always colored.	Transitional.		Ions always colored.	Trans.	Ions always colored.	Trans.	Ions always colored.
Ti 48	Cr 52	*Cu 63*	*Nb 94*	Ru 103	*Ag 108*	*Ce 142*	Di 145	*Ta 182?*	Os 192	*Ti 204*	U 240
V 51	Mn 55	----	*Mo 96*	Rh 104	------	------	Sm 150	*W 184*	Ir 192·5	*Bi 208*	-----
------	Fe 56	----	----	Pd 106	------	------	Er 169	------	Pt 194	------	------
------	Co 59	----	----	------	------	------	------	------	Au 196	------	------
------	Ni 59	----	----	------	------	------	------	------	------	------	------

The transitional elements titanium and vanadium on the one side of this series and copper on the other, are the outliers.

The second colored series contains the well known group rhodium, ruthenium and palladium. The third colored group contains the metals of the rare earths followed by the transitionals tantalum and tungsten. Finally the colored group of the platinum metals and gold. These and the remaining colored metals will be described in the next section.

One metal, zirconium, has proved rebellious to this classification.

The others have taken their places so easily and exactly that it seems as if there must be something inexact or incomplete in our data respecting this metal. The most probable supposition seems to be the following. Zirconium has but one degree of oxidation while the very closely allied metal titanium, has ions that are colored and colorless at different valencies.

Should zirconium prove to have a second degree of oxidation corresponding to colored ions, it would be brought into complete analogy with its congener and would find a place open for it in the tables.

In Table II it would take the vacant place immediately following titanium and between that metal and cerium. As a transitional metal it would take its place in Table III immediately before niobium in the second series. It is hardly necessary to remark that these are exactly the places for which its properties fit it.

All the elements contained in Table III have ions that function as kathions only.

A Periodic Law of Color.

It was necessary first to consider the elements in the great divisions into which they fall by reason of the color of their ions.

It now remains to consider the whole range of elements in one continued series from hydrogen to uranium.

Commencing with hydrogen (see Plate No. IV*) we have a double series of 18 elements with colorless ions only. Approaching one of the great colored groups which may be called the iron group we find two intermediate elements, titanium and vanadium which have both colored and colorless ions.

By their colorless ions they are united to the series which immediately precedes them in the order of numbers and by their colored ions they are united with the iron group which immediately follows. This iron group commences with the element chromium which in the numerical series immediately follows vanadium, so that after the transitionals titanium and vanadium each of which has at least one colorless ion, comes the group consisting of chromium, manganese, iron, cobalt and nickel; metals which have colored ions only.

Approaching the next colorless series we find interposed the transitional element copper, a metal having the colorless cuprous and the blue cupric ions.

From this we pass to a colorless series commencing with zinc and continuing with gallium, germanium, arsenic, selenium bromine, rubidium, strontium and concluding with yttrium. The ions of none of these elements show any tendency to color.

Continuing in numerical order the next colored group will consist of the metals ruthenium, rhodium and palladium. But in approaching these we find precisely as in the previous case two transitionals, molybdenum and niobium.

These are connected with the previous colorless group by their colorless ions and with the colored group next following by their colored ions. This colored group (Ru, Rh, Pd,) has colored ions only.

Continuing in numerical order we approach the next colorless group. But as we pass from the colored to the colorless we find as before, a transitional, in this case, silver, which is connected with the previous colored group by its colored ions corresponding with Ag_4O and Ag_2O_2† and to the following colorless group by its ion corresponding to Ag_2O.

* In the plate the third and fourth colored groups should have been on the same horizontal line as the first and second.

† The first of these colored ions is seen in the deeply colored hemi-salts of silver. Another may exist in the peroxide which dissolves in sulphuric acid with a dark green color.

From this we pass to the next colorless group of nine elements commencing with cadmium and ending with lanthanum. Approaching the next colored group we as before find a transitional element, in this case but one. At least but one is now known, but as we have now come to the region of little known metals of the rare earths it is possible that some one of those not yet thoroughly known may take its place alongside of cerium and thus bring this approach into complete symmetry with all the others.

Cerium connects itself with the colorless group immediately preceding by having colorless ions and with the colored group immediately following by its colored ions.

The colored group thus reached, composed of metals having colored ions only, consists of didymium, samarium and erbium. Then follow the transitionals tantalum (?) and tungsten.

Next, a series having ions colored at all valencies, namely osmium, iridium, platinum and gold. With gold the regular series terminates.

There follows what may be called the most curious part of the entire range of elements. This is found in the little group of six at the extreme end. In the principal series the colored groups are always immediately preceded and introduced by transitional elements, that is elements having both colorless and colored ions. The usual number of these transitionals is two. In the small final group the first two colored elements act as transitionals to the third. The first of the colored metals is thallium, this metal is allied to the alkalies by its thallious salts which are colorless; it is also closely related to the heavy metals, lead and mercury which are on each side of it. Even thallic sulphate and nitrate are colorless salts decomposed by water. But the thallic haloids form colored crystals and colored solutions and thus correspond perfectly to colored ions. Therefore thallium whilst chiefly related to the colorless elements on each side of it has nevertheless made a well-marked step towards color by its single pair of colored ions.

The next colored metal, bismuth, has advanced much further towards color, for of its four valencies all but one have colored ions. It still retains its relation however with the colorless elements on each side of it, lead and thorium, by its one pair of colorless ions corresponding to bismuth trioxide.

Finally we have the last of all the metals, uranium, with colored ions at all valencies. Standing alone it occupies as it were the position of a group to which its transitionals, thallium and bismuth, lead up, and with it the series of the elements closes.

Amongst the conclusions to be drawn from the facts that have been mentioned is this, that the color of the elementary atoms is to a large extent a *function of their atomic weights.* We find that with atomic weights,

From	1	to	47 the atoms are always colorless
From	52	to	59 they are always colored
From	65	to	90 they are always colorless
From	103	to	106 they are always colored
From	112	to	139 they are always colorless
From	145	to	169 they are always colored
From	192	to	196 they are always colored.

Elements whose place in the numerical series falls between these periods, have both colored and colorless atoms.

The six metals that remain are as we have seen, alternately colored and colorless.

Ostwald remarks in his great *Lehrbuch* that when the properties of the elements shall show themselves to be functions of their atomic weights, we have next to seek in the latter the cause of the former, and then we shall hardly be able to avoid the conception of a single primordial form of matter as suggested by Crookes, a form whose varied modes of agglomeration condition the various kinds of matter (Vol. I, p. 138).

Perhaps the facts in this paper described may be found to make a step towards this great end.

With the aid of the Arrhenius theory it has been possible to establish the principle that the colors of the atoms are those which they show in dilute solutions of electrolytes, and that the colors of elements are comparatively of little importance. In the second part of this paper there will be given incidentally a proof of the correctness of the dissociation theory from a new direction. In that part will be considered the combinations of atoms and two laws controlling in certain cases the interaction of ions.

ART. XXIX.—*Further Notes on the Gold Ores of California;* by H. W. TURNER.

SOME brief notes were published in this Journal on the gold ores of California in June, 1894, and the following may be considered as an appendix to that article.

Gold in barite.—During the past summer, the writer examined some gold veins on Big Bend Mountain in Butte County, California, and found that one of them was of an unusual

character. The vein is known as the Pinkstown ledge. It is located about a half mile due south of the highest point of Big Bend Mountain (Bidwell Bar atlas sheet). The ledge strikes N. 13° W. and dips at a high angle (about 80°). It is from two to three feet wide where best exposed at the north end, and is composed of a soft heavy mineral, some of which is coarsely crystalline, with a granular structure, but most of it is finer grained with a schistose arrangement of the granules. No single crystals of the mineral were noted having a greater maximum diameter than five-eighths of an inch. Some of them show plainly a characteristic cleavage. Dr. Hillebrand made a chemical examination of this soft mineral and reported it to be barite. Three sections of the barite were examined microscopically, and these show that when fresh there is scarcely any impurity in the mineral, and in fact no other substance was noted except scattered minute reddish opaque grains which as seen under the microscope are reddish-yellow by reflected light, without metallic luster. They may be limonite. Many of the barite grains show distinct cleavages which appear in the thin sections to intersect at nearly right angles. A tendency to a radial structure like that of epidote was noted at several points. The relief of the barite is rather high. A sample was examined for gold by Dr. Stokes, who reported that "the barite contains gold but too small in amount to be determined in the wet way." There is said, however, to be enough gold in the deposit to pay to work, and the writer understood that the owner of the ledge obtained gold from it by grinding up the ore in a hand mortar, and panning it.

A considerable part of Big Bend Mountain, as exposed along the road from the bridge over the west branch of the north fork of the Feather river to the abandoned village of Big Bend, is made up of clay slates probably Paleozoic in age, with layers of greenstone schists, representing original augitic tuffs. The rocks along the east and south base of the mountain as seen along the river (the north fork of the Feather) are almost entirely greenstones, with one or two layers of sedimentary mica-schists. These greenstones are largely amphibolitic rocks representing original surface lavas and tuffs, probably augitic porphyrites, but now containing little or no augite. The exact nature of the schist enclosing the barite vein was not determined. The south extension of the Pinkstown ledge owned by Clarke was examined but no barite was found, the rock on the dump being a white, fine grained schist, with a greasy feel. This as seen in this section is composed chiefly of minute, brightly polarizing fibers, perhaps talc, with numerous minute cubes of pyrite, arranged in rows.

Gold associated with talc-schists.—The magnesian rocks of the Sierra Nevada consist chiefly of serpentine and talc and chlorite schists. All of these rocks together with some others of similar origin are frequently found in the same area, the different varieties alternating rapidly in a perplexing manner. There are, however, especially in the area of the Bidwell Bar atlas sheet (Butte and Plumas counties) very considerable streaks of talc and chlorite-schists with little or no serpentine. It has been noted by the writer that while quartz veins are very common in the talc-schist belts, they are very rare in the serpentine. Veins containing gold and forming pocket mines do exist in the serpentine areas, but in the two examples which the writer has himself seen, there is talc-schist directly associated with the vein, forming one or both walls.

One of the veins here referred to occurs on the Downieville sheet in Sierra County, on the spur north of Rock Creek and one and a half miles east of Goodyear's Bar. Here is a small quartz vein in serpentine with talc-schist forming one wall. This vein had evidently been worked for gold, and the writer was informed that a gold pocket was found in it.

The other mine is in Mariposa County on the Mariposa Estate, and is in charge of Mr. Ludwig, who kindly showed me the deposit. There is here a streak of talc-schist in serpentine near the west border of the large belt of that rock that extends from near Princeton to Mariposa forming the high ridge just west of the latter town. The exact locality is one and three-fourths miles a little south of east from Princeton. The deposit consists besides the talc, of white dolomite looking precisely like that associated with mariposite at the Josephine Mine near Bear Valley, pyrite, and a black mineral, the latter occurring in plates with metallic surfaces in the dolomite. This black mineral was determined by Dr. W. F. Hillebrand to be titanic iron ore (ilmenite). The gold occurs native in the talc-schist, and the pyrite and ilmenite are also saved for reduction. The writer's notes make no mention of quartz in this vein.

As stated above, the talc, chlorite, and other associated schists form considerable belts in the area of the Bidwell Bar atlas sheet, and contain frequent quartz veins, as may well be seen at Quartz Hill north of Lumpkin. The writer knows of no case, however, where one of these veins has proved to be large enough and to contain enough gold to warrant the erection of a quartz-mill.

The rare occurrence of quartz veins in serpentine, a very basic magnesian rock, and their comparative abundance in talc rocks, which are much more acid, would seem to indicate a connection between quartz veins and the rock in which they form.

But as both these rocks are altered forms of deep-seated igneous rocks, it does not follow that the silica of any particular quartz vein was leached out of the wall rock and re-deposited nearly in place. These igneous masses may extend to a great depth and the ascending hot waters and gases may have been in contact with rock like the wall-rock for a long distance and for a considerable time.

As a matter of fact, quartz-veins are more common in California in sedimentary rocks which are not presumed to extend deep into the earth's crust, than in igneous masses. The cause of this is more probably a physical than a chemical one, for fissures form more readily in sedimentary than in massive igneous rocks. It is extremely likely that the sedimentary series of the Gold Belt of California is underlain throughout by granite, and that this rock is the chief source of the silica of the quartz veins in the clay slates, and other associated rocks.

Serpentine being a rock in which fissures may be supposed to form with difficulty, it is by no means improbable that there is a physical as well as a chemical reason for the lack of quartz veins in that rock.

Mariposite.—The green micaceous mineral called mariposite by Silliman occurs abundantly at the Josephine Mine near Bear Valley. Several specimens of this were obtained in 1893, and submitted to Prof. F. W. Clarke for analysis. Thin sections of the material were made and these show that the mineral is micaceous, nearly colorless or slightly greenish with brilliant polarizing colors, resembling talc. There appears to be no perceptible pleochroism. The mineral is in the form of fibers and minute irregular foils with ragged edges, and extinguishes nearly or quite parallel to the longer axis of the fibers. Macroscopically it is not all green, some of it being nearly white. Two analyses are appended by Dr. Hillebrand, one of the green, and the other of the white mineral.

Analyses of Mariposite. (*438 Sierra Nevada Coll.*)

	Green.	White.
SiO_2	55·35	56·79
TiO_2	·18	25·29
Al_2O_3	25·62	
Cr_2O_3	·18	none.
Fe_2O_3	·63	1·59
FeO	·92	
CaO	·07	·07
MgO	3·25	3·29
K_2O	9·29	8·92
$(Li\ Na)_2O$*	·12	·17‡
H_2O†	4·52	4·72
	100·13	100·84

* Very strong lithium reaction. † No water given off below 300 C.
‡ Containing some K_2O.

The thin sections show that there is carbonate, probably chiefly dolomite mixed with the mariposite. This with some carbonate of iron was extracted with acetic acid followed by warm dilute HCl, the mariposite substance remaining unattacked. Dr. Hillebrand calls attention to the resemblance of the mineral in composition to pinite, and states that no definite formula is deducible. He determined the specific gravity of the green mineral to be 2·817 at 29·5° C. and that of the white mineral to be 2·787 at 28·5° C. The occurrence of chromium in the green variety and not in the white suggest that to be the cause of the green color. While resembling talc optically it will be noted that the chemical composition is very different.

Gold quartz veins in Tertiary Rocks. — Precious metal deposits in rocks of the Tertiary period are not uncommon in the western United States. As notable examples of this may be mentioned the Comstock lode in Nevada in part at least in Tertiary lavas, and the gold and silver veins of the Bodie district in hornblende-andesite.* Silver deposits also occur in rhyolite in Southern California.† But in the Sierra Nevada gold quartz veins in any but the Paleozoic or Jura-Trias rocks are rare. The occurrence of quartz with native gold in a rhyolite dike of Tertiary age in Plumas County has already been described.‡ The gold in the Silver Mountain district in Alpine County (Markleeville atlas sheet) is in chalcedonic quartz in Tertiary andesitic tuffs and the deposits of the Monitor district are likewise in Tertiary volcanic rocks. One of the ore specimens given the writer by Judge Arnot as coming from the last district is chalcedonic quartz containing gold. In both these districts the rocks containing the deposits are much decomposed by solfataric action, and both are on the east slope of the range in the Great Basin drainage.

About one and a half miles south of La Grange in Stanislaus County (Sonora atlas sheet) in a flat-topped hill there are abundant veins of white quartz in clay which appears at first glance to be the basal portion of the Tertiary clastic series that caps the hill. Overlying the clay is a sandstone containing pebbles of white quartz and pearly scales of a hydrous silicate of alumina, which is very abundant in the Ione sandstone.§ The age of the sandstone is thought to be Miocene. Portions of the underlying clay are white in color, other portions stained pinkish in streaks and patches. When first visited, some years ago, the clay appeared to the writer to represent the

* This was first noted by Mr. W. Lindgren.
† W. Lindgren, Trans. Am. Inst. Mng. Eng., February, 1887.
‡ This Journal, vol. xlvii, p. 472.
§ American Geologist, vol. xiii, p. 240.

lower clay of the Ione formation, which is well exposed at Ione and elsewhere, and as the quartz veins are unquestionably in the clay it was then thought that the quartz veins were of Tertiary age. The quartz is the white, compact kind that occurs in the majority of the gold quartz veins, and not the chalcedonic quartz known to exist in veins in Tertiary rocks.

On a second visit to the locality in 1894, good evidence was found that the clay is but the decomposed bed rock, which is here a quartz-porphyrite. Pebbles of the hardened clay were found in the lower part of the sandstone and along some sharp contacts of the clay and overlying sandstone it was noted that the quartz veins stopped short at this contact. No quartz veins were found with certainty in the sandstone itself. Moreover some cracks in the clay extending down from its upper surface were filled with the material of the sandstone, showing that these cracks were in existence when the sandstone was being deposited and were filled in from above. At the head of a little gulch on the west side of the hill is a good exposure of the clay with numerous quartz veins. The latter have a varying course dipping mostly north at angles from 10° upward, some veins curving very noticeably in a vertical direction. In some of this much stained and discolored clay, porphyritic quartzes are to be seen, and as lower down in the gulch there is little altered quartz-porphyrite in place, there seems little question that the clay is a decomposed form of the same rock. At other points, notably on the east side of the hill the white clay shows no evidence of its derivation from the bed rock, being of even texture throughout and without discolora tion. Slickensided surfaces were noted in the clay at several points, along seams that intersect at varying angles.

Tetrahedrite.—This sulphide of copper and antimony has not often been noted by the writer in the gold ores of the Sierra Nevada. What appears to be this mineral, however, occurs very abundantly in the quartz veins of Mono Pass, east of the Yosemite Valley. The specimens (No. 455 S. N. collection) collected there by the writer from the Golden Crown ledge were examined by Prof. R. L. Packard, who reported that the sulphide is tetrahedrite or an allied mineral giving blowpipe reactions for sulphur, antimony, copper, lead and iron. The ore is presumed to contain silver and perhaps gold, but neither of these were determined.

Mr. W. Lindgren informs me that he has detected tetrahedrite at the following mines: The Boulder, Hathaway, Golden Stag, and Pine Tree mines in the Ophir district in Places County; the Osborne Hill mine at Grass Valley, Nevada County; and the Miller & Holmes, Knox & Boyle, and Whiskey Hill in Tuolumne County, azurite being associated with the tetrahedrite in the last three mines.

Tioga mining district.—This is situated to the northwest of Mono Pass in the same body of schists that occurs in the pass. Some specimens obtained here in 1886 by the writer from the Isbell claim on Lee Vining Creek. These were assayed by Dr. W. H. Melville with the following results:

No. 876 Sierra Nevada Collection—

a: chiefly made up of zinc blende; contains 5 oz. gold and 7 oz. silver to the ton.

b: largely iron and copper pyrites; contains a trace of gold, and nearly 16 oz. silver to the ton.

c: contains a large amount of arsenical pyrite, 51 oz. gold and 32 oz. silver to the ton.

The above samples probably do not represent an average of the ore and are merely given to show the association of minerals in the vein.

Washington, D. C.

ART. XXX.—*On Some Relations between Temperature, Pressure, and Latent Heat of Vaporization;* by C. E. LINEBARGER.

THE well-known equation

$$\frac{dp}{dT} = A\frac{\rho}{T(v-v')}, \text{ or } \frac{dp}{dT} = A\frac{\rho}{Tdv}, \qquad (1)$$

in which p is the pressure; T, the temperature; ρ, the latent heat of vaporization; v, the volume of the saturated vapor; and v', that of the liquid, may be considered to resume most of the relations between temperature, pressure, and latent heat of vaporization; it expresses fundamental relationships between heat,—and volume-energy, as is at once seen, when it is thrown into the form:

$$dp\, dv = A\rho\frac{dT}{T}, \qquad (2)$$

an equation of which the left-hand member contains only the factors of volume-energy, and the right-hand member only those of heat-energy. But certain relationships between these factors of energy were found out quite independently of the fundamental equation; guided by no theoretical considerations, their discoverers, by scrutinizing experimental data, saw some regularities which, when generalized, became laws, although approximate and containing inexplicable anomalies. Also, the

differential forms of equations (1) and (2) do not readily permit of direct comparison with empirical facts; they must first by suitable hypotheses and integrations be thrown into other forms. The comparison of the deductions and discovered relationships with the experimental data generally shows a close correspondence. Sometimes, however, variations and exceptions occur which cannot be referred to experimental errors.

The object of this paper is to give an account of the efforts that have been made and the results that have been obtained in regard to the relations between pressure, temperature, and latent heat of vaporization; to subject to a critical revision all experimental data bearing upon the question; to discuss the differences seemingly present between theory and experiment; and to apply the results to certain practical problems. The division of the matter is the following: first, a historical account of such papers as have dealt with the theoretical side of the question; second, a review in tabular form of experimental data together with a discussion of their comparative value; third, a comparison of the results of theory and experiment; fourth, an application of results to a practical problem.

I.

The first paper in which an endeavor was made to find out relations between latent heats of vaporization and other energy-factors is due to Ure;* this pioneer in this field of research determined the heats of vaporization of a number of common liquids, and concluded from his results that under the same pressure the latent heat of vaporization is inversely proportional to the vapor density.

Desprets,† in a paper read before the French Academy towards the end of the year 1818, but of which merely an abstract seems ever to have been published, communicated the results of some determinations of the latent heats of vaporization of water, alcohol, ether, and essence of terebinthine. An inspection of his data led him to state that a liquid at its point of ebullition requires for volatilization so much the less heat, the denser its vapor; latent heats of vaporization are approximately proportional to densities at the boiling points.

Person‡ after determining the latent heats of vaporization of ten additional liquids, notwithstanding that his results were not as accurate as those of Desprets, as he himself admits, and without giving any data, formulated a law, which is "for the heat of vaporization what the law of Dulong and Petit is for the specific heat," and "even more general, since it applies to

* Phil. Mag. liii, 191, 1819.
† Ann. Chim. et Phys., xxiv, 323, 1823.
‡ Comptes Rend., xvii, 498, 1843.

simple and to compound bodies without distinction." This law is: "The heats of vaporization of different substances range themselves exactly in the order of their temperatures of ebullition, when, instead of equal weights, atomic weights are taken. In a "Note" three years later Person* reverts to his law, and drawing up a table of latent heats of vaporization from the data due to Favre and Silbermann shows how well his previous statements are corroborated by these determinations. The exceptions presented by the acids are explained away by making allowance for their abnormal vapor densities. In this paper, he puts his law in a somewhat different form: "The amount of heat needed to vaporize substances under the same pressure is identical, when the volume produced is the same, and it is smaller or greater according as the volume produced is smaller or greater."

Trouton† "on comparing the quantities of heat necessary to evaporate at constant pressure quantities of different liquids taken in the ratio of the molecular weights,"—found that the amount of heat required by any body is approximately proportional to its absolute temperature at the point of ebullition." He then propounded the following law:" The molecules of chemically related bodies, in changing from the gaseous to the liquid state at the same pressure, disengage quantities of heat, which may be called the molecular latent heat, directly proportional to the absolute temperature of the point of ebullition."

The above laws are purely empirical; they were found through observation of rows of figures; they have no theoretical grounding; being subject to exceptions and irregularities, they can never as deduced rise to the rank of great generalizations; they have been drawn up by the inspection of experimental data, which is an inversion of the usual order of discovery, experimental data as a rule being a means of corroboration rather than of deduction of laws of nature.

We now pass to the consideration of the work that has been done along theoretical lines in the finding out of relations between heat of vaporization, temperature, and pressure.

The first effort made in this direction is due to Raoul Pictet, in a paper truly remarkable for its time, although it seems to have attracted but little attention. Pictet considers a cycle in which a liquid is evaporated from one chamber, condensed in another, and finally returned to the first. Admitting the validity for the case in hand of the laws of Boyle and Gay-Lussac, he then finds mathematical expressions for the work done and the heat absorbed. In order to equate these essen-

* Comptes Rend., xxiii, 524, 1846.
† Phil. Mag., V., xviii, 54, 1884.

tially independent expressions he makes two hypotheses: 1, the cohesion of liquids is the same for all: 2, Carnot's cycle is applicable to volatile liquids, and to their changes of volume: and there exists a relation between heat taken in and work performed. The expressions finally arrived at show a satisfactory correspondence for the most part with the determinations of latent heats of vaporization made by Regnault. The conclusions which have a bearing upon our subject are: I—The product of the latent heats of liquids at the same pressure by their atomic weights, divided by the absolute temperature at which the vaporization takes place, is the same for all: II—The difference between the internal heats of vaporization at any two temperatures, multiplied by the atomic weights, is a constant number for all liquids.

We will not enter into any discussion of these results, contenting ourselves with remarking that the first conclusion is a plain enunciation of "Trouton's law" mentioned above. If priority of publication has any moment in the choice of the name of a discovery, the law in question ought to be called Pictet's law since the date of Pictet's paper is 1876 and that of Trouton's 1884.

Equation (1) seems first to have been made use of by van der Waals* for the establishing of relationships between temperature, pressure, and latent heat of evaporation. If for p, T, and v, εp, $m T_1$, and $\varphi(m)\frac{b}{v}$ (p_1 being the critical pressure, T_1, the critical temperature, b, the covolume, and ε, m, $\varphi(m)$, coefficients) be substituted in equation (1), and it be kept in mind that

$$\frac{v\mu}{b} = f(m),$$

(μ being the molecular mass), the equation

$$\frac{d\varepsilon}{dm} = \frac{8{\cdot}273}{A} \cdot \frac{\rho\mu}{T_1} \cdot \frac{1}{\varphi m} \qquad (3)$$

or

$$\frac{d\varepsilon}{dm} = C \cdot \frac{\rho\mu}{T_1} \cdot \frac{1}{\varphi} \qquad (4)$$

results. Now when m is the same, that is, at the same reduced temperature, $\frac{d\varepsilon}{dm}$ must have the same value, and as a necessary consequence it follows that

$$\frac{\rho\mu}{T_1} = F(m) \qquad (5)$$

* Continuität des gasförmigen und flüssigen Zustandes, p. 137.

where F is a constant number for all bodies. But equation (5) is nothing else than the mathematical expression for "Trouton's law," and again the rightfulness of this name may be justly questioned, for the German translation of van der Waal's book appeared three years before Trouton's paper. Van der Waals called to mind the similarity of the expression as developed just above to the law proposed by Desprets (loc. cit.), and drew up a little table of data to see if experiment corroborated theory, which in a certain measure he found to be the case.

Bouty* sought to transform the fundamental equation (1) so as to get the quotient of the molecular heat of vaporization by the square of the absolute temperature equal to a constant. His course of reasoning is as follows. If, in the formula

$$\rho = \mathrm{T}(v-v')\frac{dp}{d\mathrm{T}} \tag{6}$$

the specific volume of the liquid be neglected in comparison with that of the vapor, and if the density of the latter be normal, it ensues that

$$v = \frac{1}{\mathrm{D}\mu}\frac{p_0}{p}\cdot\frac{\mathrm{T}}{273}, \tag{7}$$

where D is the absolute specific gravity of hydrogen at the temperature zero and under the pressure of 760^{mm} of mercury. By the combination of (6) and (7) the equation

$$\rho\mu = \frac{p_0}{273\mathrm{D}_0}\frac{\mathrm{T}^2}{p}\frac{dp}{d\mathrm{T}} \tag{8}$$

is obtained; and if T_0 be the boiling point under the pressure p_0,

$$\rho\mu = \frac{\mathrm{T}_0^2}{273\mathrm{D}}\left(\frac{dp}{d\mathrm{T}}\right)_0. \tag{9}$$

If it be admitted with Dalton that all vapors have the same tensions at temperatures equidistant from the boiling points of the liquids which give them off, the expression

$$\left(\frac{dp}{d\mathrm{T}}\right)_0$$

must be the same for all liquids, and the expression

$$\frac{\rho\mu}{\mathrm{T}_0^2} \tag{10}$$

becomes equal to a constant.

Although Bouty is inclined to admit that Dalton's "law" is incorrect, and hence (10) cannot be constant, he gives a table of "constants" for a number of liquids, of which, as de Heen

* Journ. de Phys., II, iv, 26.

remarks* "it is needless to say that the variations to be found in the values of $\frac{\rho\mu}{T^2}$ are enormous." If, however, it be assumed that $T\frac{dp}{dT}$ be constant,† it at once follows that $\frac{\mu\rho}{T}$ = constant, which is Trouton's or better Pictet's law.

Le Chatelier‡ also has transformed equation (1) into another directly comparable with the results of experiment. After putting it in the form

$$\frac{\rho}{T}dT + A(v-v')dp = 0, \tag{11}$$

(ρ in Le Chatelier's calculations is always taken to be the *molecular* heat of vaporization) by multiplying and dividing the second term by p, he obtained this expression

$$\frac{\rho}{T}dT + Ap(v-v')\frac{dp}{p} = 0 \tag{12}$$

If the volume of the liquid be neglected in comparison with that of the vapor, and the gas equation

$$pv = RT$$

be introduced, after division by T, the expression

$$\rho\frac{dT}{T^2} + AR\frac{dp}{p} = 0 \tag{13}$$

or

$$\rho\frac{dT}{T^2} + 2\log p = 0 \tag{14}$$

is obtained. If this equation be integrated between the limits T and T_0, it being admitted that the heat of vaporization is constant, the equation

$$2\int_{T_0}^{T}\frac{dp}{p} + \int_{T_0}^{T}\rho\frac{dT}{T_2} = 0 \tag{15}$$

results, and, all calculations being made on the assumption that ρ is independent of T,

* Bulletin de l'Académie royale de Belgique, III, ix, p. 281, 1885.

† The results of Ramsay's and Young's experiments show that $T\frac{dp}{dT}$ is constant for considerable differences of pressure. If it be true that $T\frac{dp}{dT}$ is constant then $\frac{\rho}{dv}$ must be constant also, for

$$\frac{dp}{dT}\cdot\frac{T}{A} = \frac{\rho}{dv}.$$

Ramsay and Young have also experimentally proven the truth of this relation. See Phil. Mag., V, xx, p. 515, 1885; ibid., xxi, pp. 33 and 135; and ibid., xxii, p. 33, 1886.

‡ Recherches expérimentales et théoriques sur les equilibres chimiques, Ann. des Mines, Mars–Avril, 1888, p. 337.

$$2 \log \frac{p}{p_o} + \rho\left(\frac{1}{T} - \frac{1}{T}\right) = 0. \qquad (16)$$

This equation contains no constant, but if the terms T_o and p_o, which together form a constant, be transferred to the second member, the equation

$$2 \log p + \frac{\rho}{T} = \text{constant} \qquad (17)$$

is obtained, and if the pressure be kept constant.

$$\frac{\rho}{T} = \text{constant}, \qquad (18)$$

or, if ρ be taken as the heat of vaporization of the unit of mass of liquid,

$$\frac{\mu\rho}{T} = \text{constant}. \qquad (18 \text{ bis})$$

It is seen from the foregoing that the constancy of the quotient of the molecular heat of vaporization by the absolute temperature at which the vaporization takes place has been arrived at by various scientists in different ways. This in itself is strong warrant for the truth of the relation. Still there exist certain discrepancies between the theory and the experimental determinations, which must be accounted for. Before taking up their consideration, however, it is necessary to pass in review what experimental work has been done.

II.

In Table I are given the latent heats of vaporization of a number of liquids, which have been determined by direct experiment at or near the ordinary atmospheric pressure. Only such liquids as are chemical units are admitted, solutions of acids and the like being excluded; also the determinations made with very volatile liquids, such as ammonia, sulphur dioxide, etc., are omitted. With these exceptions it is believed that no omissions of importance have been made.

The first column refers to the "References;" the second column (*a*) gives the name of the liquids; the third (*b*) their formula, and the fourth (*c*) their molecular masses; in the fifth (*d*) and sixth (*e*) columns are contained the temperatures at which vaporization took place and the latent heats for one gram of the liquid in heat units of which one warms one gram of water from 0° to 1° C., while the seventh (*f*) column shows the quotient obtained by dividing the molecular heat of vaporization by the absolute temperature. The eighth column (*g*) gives the pressure in rounded millimeters of mercury; when the pressure has not been indicated by the investigator, the space has been left vacant; however, from the nature of the methods, the pressure cannot vary greatly from normal atmospheric pressure.

TABLE I.

	Name.	Formula.	Molecular Mass.	Temp.	Latent Heat.	$\frac{\mu\rho}{T_{abs}}$	Pressure.
	a	*b*	*c*	*d*	*e*	*f*	*g*
I	Bromine	Br_2	160	58	45·6	22·04	752
XIV	"	"	160	61·6	43·7	20·95	----
XX	Sulphur	S_x	32*x*	316	362·0	19·66	760
XX	Mercury	Hg	200	350	62·0	19·90	760
I	Phosphorus chloride	PCl_3	137·3	78·5	51·4	20·07	750
I	Tin tetrachloride	$SnCl_4$	259·5	112·5	30·5	20·49	753
XVIII	*Sulphur chloride	S_2Cl_2	135	136	49·4	16·30	----
I	Carbon bisulphide	CS_2	76	46·2	86·7	20·64	758
XXVIII	" "	"	76	46·1	83·8	19·96	----
XXIV	" "	"	76	46·6	85·7	20·37	759
XVIIa	Diethylamine	$C_4H_{11}N$	73	58	61·0	20·07	----
IV	*Amylene	C_5H_{10}	70	12·5	75·0	18·49	----
XXVI	Benzene	C_6H_6	78	80·35	93·4	20·63	765
XXVIII	"	"	78	80·1	92·9	20·50	----
XXVI	Toluene	C_7H_8	82	110·8	83·6	20·02	765
XXVI	Ethylbenzene	C_8H_{10}	106	134·7	76·4	19·86	757
XXVI	Propyl benzene	C_9H_{12}	120	157·0	71 8	20·00	754
XXVI	Metaxylene	C_8H_{10}	106	139·9	78·3	20 09	766
XXVI	Pseudocumol	C_9H_{12}	120	168·0	72 8	19·58	764
XXVI	Cymol	$C_{10}H_4$	134	175·0	66·3	19·83	755
XI	Methylene chloride	CH_2Cl_2	84·7	41·6	75·3	20·25	----
XXVIII	Chloroform	$CHCl_3$	119·1	60·9	58 5	20·84	----
XXVIII	Carbon tetrachloride	CCl_4	153·6	76·4	46·4	20·35	----
XXIII	" "	"	153·6	76·4	46·6	20·49	758
I	Methyl iodide	CH_3I	141·5	42·2	46·2	20·66	751
XI	Ethylidene chloride	$C_2H_4Cl_2$	98·7	60	67·0	19·88	----
XXIV	Ethyl chloride	C_2H_5Cl	64·4	21·17	89·3	19·59	----
XXVIII	" bromide	C_2H_5Br	109	38·2	60·4	21·15	----
VIII	" "	"	109	38·4	61·6	22·25	----
I	" iodide	C_2H_5I	155·5	71·3	46·9	21·16	742
VIII	Ethylene bromide	$C_2H_4Br_2$	188	131	43·8	20·38	----
VIII	*Amyl chloride	$C_5H_{11}Cl$	106·5	107	56·3	15·78	----
VIII	*Amyl bromide	$C_5H_{11}Br$	151	129	48·3	18·14	----
VIII	*Amyl iodide	$C_5H_{11}I$	197·5	156	47·5	21·87	----
I	*Methyl formiate	$C_2H_4O_2$	60	32·9	117·1	22·96	752
X	* " "	"	60	33(?)	115·2	22·58	----
I	*Ethyl "	$C_3H_6O_2$	74	54·3	105·3	26·86	752
X	* " "	"	74	53·5(?)	100·4	22 75	----
XXVI	" "	"	74	53·5	92·2	20 88	753
XXVI	Propyl "	$C_4H_8O_2$	88	81·2	85·3	21.18	760
XXVI	Isobutyl "	$C_5H_{10}O_2$	102	98·0	77·0	21·17	759
XXVI	Isoamyl "	$C_6H_{12}O_2$	116	124·0	71·7	20·93	759
XXVI	Methyl acetate	$C_3H_6O_2$	74	57·3	94·0	21·04	757
I	* " "	"	74	55·0	110·2	24·86	----
I	*Ethyl "	$C_4H_8O_2$	88	74·6	92·7	23·46	----
XXVI	" "	"	88	77·0	83·1	20·88	760
XXVIII	" "	"	88	73·1	84·3	21·43	----
XXVI	Propyl "	$C_5H_{10}O_2$	102	102·3	77·3	21·00	760
XXVI	Isobutyl "	$C_6H_{12}O_2$	116	116·8	69·9	20·83	761
XXVI	Isoamyl "	$C_7H_{14}O_2$	130	142·0	66·4	20·78	757
XXVI	Methyl propionate	$C_4H_8O_2$	88	80·0	84·2	20·97	760
XXVI	Ethyl "	$C_5H_{10}O_2$	102	98·7	77·1	21·15	759

TABLE I—*Continued.*

	Name.	Formula.	Molecular Mass.	Temp.	Latent Heat.	$\frac{\mu\rho}{T_{abs}}$	Pressure.
	a	*b*	*c*	*d*	*e*	*f*	*g*
XXVI	Propyl propionate	$C_6H_2O_2$	116	122·6	71·5	20·96	759
XXVI	Isobutyl "	$C_7H_{14}O_2$	130	136·8	66·0	20·96	760
XXVI	Isoamyl "	$C_8H_{16}O_2$	144	160·5	63·1	20·94	755
XXVI	Methyl butyrate	$C_5H_{10}O_2$	102	102·3	77·3	20·70	760
XXVI	Ethyl "	$C_6H_{12}O_2$	116	119	71·5	21·15	751
XXVI	Propyl "	$C_7H_{14}O_2$	130	143·6	66·2	20·65	761
XXVI	Isobutyl "	$C_8H_{16}O_2$	144	156·7	61·9	20·74	756
XXVI	Isoamyl "	$C_9H_{18}O_2$	158	178·0	59·4	20 80	761
XXVI	Methyl isobutyrate	$C_5H_{10}O_2$	102	92·5	75·5	21·06	757
XXVI	Ethyl "	$C_6H_{12}O_2$	116	110·0	69·2	20·96	758
XXVI	Propyl "	$C_7H_{14}O_2$	130	134·0	63·9	20·36	759
XXVI	Isobutyl "	$C_8H_{16}O_2$	144	148·6	59·9	20·47	760
XXVI	Isoamyl "	$C_9H_{18}O_2$	158	168·0	57·7	20·65	758
XXVI	Methyl valerate	$C_6H_{12}O_2$	116	116·3	69·9	20·83	758
XXVI	Ethyl "	$C_7H_{14}O_2$	130	134·0	64·7	20·67	758
XXVI	Propyl "	$C_8H_{16}O_2$	144	155·5	61·2	20·56	758
XXVI	Isobutyl "	$C_9H_{18}O_2$	158	169·0	57·9	20·69	760
XXVI	Isoamyl "	$C_{10}H_{20}O_2$	172	187·5	56·2	20·99	763
I	*Ethyl oxalate	$C_6H_{10}O_4$	146	184·4	72·7	23·22	756
XI	Ethylene oxide	C_2H_4O	44	13·5	138·6	21·28	....
XV	Ethyl oxide	$C_4H_{10}O$	74	34·9	89·9	21·63	....
I	" "	"	74	34·9	90·5	21·75	....
XXVIII	" "	"	74	34·5	88·4	21·27	....
XXII	" "	"	74	34·8	84·5	20·31	....
	Methylal	$C_3H_8O_2$	76	42·0	89·9	21·54	....
XVII	Water	$(H_2O)x$	18_x	99 8	535·8	25·87	....
I	"	"	18_x	100	535·9	25·85	760
XXV	"	"	18_x	100	532·0	25·67	....
XXVIII	Methyl alcohol	$(CH_4O)x$	32_x	64·5	267·5	25·36	....
XVII	" "	"	32_x	66·5	263·9	24 87	....
XVII	Ethyl "	$(C_2H_6O)x$	46_x	78·4	208·9	27·34	....
I	" "	"	46_x	77·9	202·4	26·53	759
XXV	" "	"	46_x	78·0	206·4	27·04	....
XXVIII	" "	"	46_x	78·1	205·0	26·85	....
XIXa	" "	"	46_x	78·3	201·4	26·37	....
XIXa	Propyl "	$(C_3H_8O)x$	60_x	96·9	164·1	26·61	....
XIXa	Isopropyl "	$(C_3H_8O)x$	60_x	82·2	159·7	26·98	....
XIXa	Butyl " (nor)	$(C_4H_{10}O)x$	74_x	116·5	138·2	26·25	....
XIXa	Isobutyl "	$(C_4H_{10}O)x$	74_x	107·7	136·2	26·47	....
XVII	Amyl "	$(C_5H_{12}O)x$	88_x	131(?)	121·4	26·44	....
XXV	" "	"	88_x	131	120·0	26·13	....
XIXa	" "	"	88_x	130·1	118·2	25·79	....
	Dimethylethyl carbinal	$(C_5H_{12}O)x$	88_x	102·1	110·4	25·90	....
XVII	Cetyl alcohol	$(C_{16}H_{34}O)x$	242_x	360(?)	58·5	22·36	....
XXVIII	Acetone	$(C_3H_6O)x$	58_x	56·6	125·3	22·05	....
XVII	Formic acid	$(CH_2O_2)x$	46_x	100	120·7	14·88	....
X	" "	"	46_x	100	103·7	12·78	....
XIII	Acetic "	$(C_2H_4O_2)x$	60_x	118	84·9	13·03	....
XVII	Butyric "	$(C_4H_8O_2)x$	88_x	164	114·7	23·09	....
XVII	Valeric "	$(C_5H_{10}O_2)x$	102_x	175	103·5	23 57	....
XIa	Nitromethane	$C_1H_3NO_2$	60	101	116·7	18·71	....
XIa	Nitroethane	$C_2H_5NO_2$	75	113	92·0	17·72	....

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It is not easy to make an estimate of the accuracy of some of the data recorded in the foregoing table; the determinations have been made by scientists employing different methods and different preparations, and hence the same degree of exactitude cannot be attributed to the work of each. Two principal sources of error are encountered in the determinations of latent heats of vaporization: the method may not be accurate: the liquid may not be pure. As a rule, in the same investigation both these sources of error are met with; that is, those investigators who have worked by faulty methods have also not always taken liquids of requisite purity. Nearly all the earlier determinations are subject to this criticism, as those by Person, Brix, and, to some extent, especially as regards the purity of the products, those by Favre and Silbermann. Andrews' work which, as far as the method is concerned, is remarkably accurate for the time when it was done, has been performed in some cases with impure liquids; this is especially true of the ethers investigated by him. Schiff states how difficult it is to obtain in a state of great purity the more volatile ethers. Thus, for ethyl formiate, a liquid very hard to purify, Schiff found the heat of vaporization to be 92·15 cal., while Andrews found 105·3 cal. With the exception of the ethers, however, Andrews' determinations may be regarded as very precious data. Of the purity of the liquids used by Berthelot and by Ogier, it is especially hard to form an opinion, inasmuch as these scientists have not indicated with but few exceptions

their methods of purification. If it be permitted to judge from a single example taken at random, we cannot admit that their products were always as pure as necessary; thus, they found for the latent heat of vaporization of ethyl formiate, which, as stated just above, Schiff determined to be 92·15 cal., equal to 100·4 cal. The impurity within compounds of the ether class is for the most part water. Since water requires much more heat for vaporization than most liquids, its presence, even in minimal amount, exercises considerable influence upon the value of a determination. In those cases, therefore, where water may be present as impurity, the heat of vaporization will be too high. And, as a matter of fact, the determinations on the ethers made by Andrews, as well as by Berthelot and by Ogier, all give values higher than those found by Schiff, who took the greatest pains to fully rid his preparations of water. The method employed by them is, however, quite beyond any but the sharpest criticism, so that their determinations may be admitted as sufficiently accurate with the exception of the amyl halogen compounds, amylene, ethyl formiate, and sulphur chloride. The work of the other investigators may be admitted without question, especially that due to Schiff, which is a marvel of accuracy. Such determinations as are not trustworthy are marked in the table with a star.

III.

An inspection of Table I shows that the numbers in column *f* are quite constant, with the exception of the alcohols, the acids, and the nitro-compounds, as well as water and acetone. Leaving these liquids aside for a moment,—their seemingly irregular behavior will be explained away later on—we will consider the various family of compounds of which Table I is made up. Taking all the reliable determinations into consideration, we find that the average value of the "constant" is for about seventy liquids equal to *20·70*, the greatest value being 22·04 for bromine (Andrews I).* For the elements and inorganic compounds, the "constant" is equal to *20·41* with 22·04 and 19·66 as extreme values; for the hydrocarbons, to *20·19*, 20·63 and 19·58 being the extreme values; for the halogen compounds, to *20·63*, with extreme values equal to 21·16 and 19·59; for the esters, to *20·87*, the extremes being 21·43 and 20·36. With the exception of the esters, the determinations have been made by different men in different ways, so that a great degree of "constancy" is hardly to be expected; yet the

* The determination by Berthelot and Ogier (xiv), however, gives 20·95 as the value of the "constant," so that it is perhaps better to reject Andrews' determination. If that be done the greatest value is 21·54 for methylal (Berthelot) and the smallest value being 19·58 for pseudocumene (Schiff).

"constant" is remarkably constant. Schiff's work was most carefully done by the same method and hence his results are at once reliable and comparable in an eminent degree; and, as a matter of fact, the extreme values of the constant calculated from his data differ from the average value by hardly three per cent.

Such a regularity as the above implies that the liquids at their boiling points are in corresponding states (the term "corresponding states" being used in the sense given it by van der Waals (loc. cit.) As far as the pressure is concerned, it may be stated that atmospheric pressure can be reckoned as "corresponding" in questions of this sort. That boiling points for certain properties of liquids are "corresponding temperatures" in a not inconsiderable measure has been shown by C. M. Guldberg* who in comparing the quotient of the absolute boiling points by the absolute critical temperature found it to remain close to an average value of about $\frac{2}{3}$, and concluded that quantities which vary slowly with the temperature (among which latent heats of vaporization are to be counted) may be reckoned as being approximately in corresponding states at their points of ebullition. This conclusion follows directly from equation (4) which indicates that the relation

$$\frac{\rho\mu}{T_1} = \psi\frac{T}{T_1} \qquad (19)$$

must obtain (ψ being an unknown function). Guldberg then states that through comparison of various liquids the equation

$$\psi(\tfrac{2}{3}) = 14 \qquad (20)$$

is found by means of graphic interpolation, and accordingly at the boiling points the relation

$$\frac{\rho\mu}{T_1} = 14 \qquad (21)$$

obtains with a certain approximation. Inasmuch as

$$\frac{T}{T_1} = \tfrac{2}{3},$$

it follows that

$$\frac{\rho\mu}{T} = 21. \qquad (22)$$

Guldberg thus obtains about the same "constant" as has been shown in the foregoing to be the average of reliable determinations.

As stated above, the values of $\frac{\mu\rho}{T}$ given in the table differ

* Zeitschr. für phys. Chemie, v, p. 374, 1890.

considerably from the normal average value in the case of the acids, nitro-methane and nitro-ethane, the alcohols, acetone and water. For the acids and nitro-compounds they are too small; for the alcohols, water, and acetone, they are too large. The cause of this abnormal behavior is to be found in the "association" of the molecules of these liquids, and in the changes which the molecular aggregations undergo during the process of vaporization. We will consider the case of the alcohols, water, and acetone first.

The brilliant experiments of Ramsay and his associates on the surface tensions of liquids, and his theoretical deductions have taught us that the liquids in question are made up of molecules in a state of association. No facts are known, however, which indicate that an appreciable amount of molecular association is persistent in the vaporous state; on the contrary, the normality of the vapor density, and other properties of the vapors, show that they consist exclusively, it may be said, of simple molecules. Accordingly, when the alcohols, etc., are evaporated, there occurs a decomposition of the complex molecules into simple ones. This requires the expenditure of a certain amount of energy, which is manifest as heat energy. The heat necessary to convert a molecularly polymerized liquid into its normal vapor consist then of two terms,* the heat expended in actually turning the liquid into a gas, and the heat used up in decomposing the molecular aggregations or "tagmas." The value of ρ, then, in the expression $\frac{\rho\mu}{T} = \text{const.}$ is greater for associated than for normal liquids; hence the value of the "constant" becomes greater, and, indeed, so much the greater, the more complex the liquid molecule. It seems at present impossible to make a reliable correction for the heat employed in decomposing the complex molecules.

In the case of the acids, the state of affairs is somewhat different. It has long been known that the organic acids, as formic, and acetic acid, have abnormal vapor densities due to the association of the molecules in the vaporous state; as the temperature rises, the degree of association becomes less and less until the normal molecule is reached. At the boiling points under ordinary atmospheric pressure, the vapor density of formic acid may by extrapolation from the data due to Petersen and Ekstrand† be put at 2·5 at 100°; this multiplied by 28·87 gives a molecular mass of 72; and this value of μ when introduced into the relation $\frac{\mu\rho}{T_{abs}} = \text{const.}$, gives for the

* See Guye's paper: Sur la polymirisation moléculaire des liquides: Archives des Sciences physiques et naturelles, III, xxxi, 160, 1894.

† Ber. der deutschen chem. Gesell., xiii, 1194.

"constant," *19·89*. Likewise from extrapolation of Cahours* determinations of the vapor density of acetic acid, its vapor density at 118° may be set at 3·3, which by multiplication by 28·87 gives as molecular mass 95; and this in turn shows the value of the "constant" to be *20·34*. Now we have every reason to believe that the gaseous associated molecule does not dissociate on passing into the liquid state; on the contrary, there can scarcely be any doubt but that it increases more or less in complexity. Accordingly, the molecular masses calculated for the gaseous molecules may be set as very near those of the liquid molecules of the two acids in question, and, indeed, the experiments of Schall† indicate that for acetic acid, at least, such is the state of affairs. The values of the "constant" found for these corrected molecular masses are seen to be practically identical with that found for normal liquids, and the exception presented by the acids is seen to be but seeming. For butyric and valeric acids, however, the "constants" cannot be corrected as for the two preceding acids, since they are found to be too large even when calculated on the assumption that their molecular masses are normal. If their determinations of latent heat of volatilization are sufficiently accurate—which is somewhat doubtful—it is probable that the complex liquid molecules in their case undergo decomposition on passing into the vaporous state, similar to the alcohols, etc. In the absence of experiments on their vapor densities it is not possible to judge what is the true state of the case.

Nitromethane and nitroethane also give values of the constant less than the normal. Ramsay and Shields‡ have measured the superficial tension of nitroethane, finding it such as to legitimatize the assumption that the molecules of this liquid are in a state of association; by analogy it may be admitted that nitromethane is also an associated liquid, although no experimental data are at hand. If what has been said in explanation of the seeming abnormality in the behavior of the acids as regards the "constant" be in accordance with fact, it is necessary to suppose that the two nitro-compounds also pass from the liquid into the gaseous condition without the complex molecule suffering much dissociation.

The immediately preceding considerations indicate a method of getting an approximation of the degree of association of a liquid. If any liquid, whose latent heat of volatilization be known, gives a value for the "constant" close to 20·7, it is pretty certain that it is normal. If it gives a less value, it is associated in the liquid as well as in the gaseous state; if it

* Comp. Rend., xix, 771.

† Ber. der deutschen chem. Gesell., xvii, 2199, 1884.

‡ Zeitschr. für phys. Chem., xii, 433, 1893.

gives a greater value, it must be associated in the liquid state alone. The greater the variation from the normal value of the "constant," the greater the amount of the association.

Thus far, we have considered the application of the formula $\frac{\mu\rho}{T_{abs}} = \text{const.}$ only to determinations made under the pressure of about one atmosphere. But how will it be at other pressures and hence other temperatures? All of the deductions of the formula have been made on the assumption that the pressure was that of one atmosphere, with the exception of the one developed by Le Chatelier, which contains a term referring to pressure (Equation 17). This equation, however, was derived on the supposition that the latent heat of vaporization is independent of temperature and pressure; such an assumption, however, does not accord with the experimental results obtained by Regnault, Ramsay and Young, Jahn, and others. The heat of vaporization of a liquid decreases with rise of temperature and concomitant increase of pressure until at the critical point it becomes equal to zero. Yet for all temperatures and concurrent pressures below the critical, the relation (17) obtains, and the lower the temperature, the larger the "constant." The number of reliable data at hand for the comparison of the theory with experiment at other pressures than the atmospheric is relatively small. Most of them have been made at the freezing point of water under the pressure of the saturated vapor at that temperature. In Table II are given such data as are reliable, and only for normal liquids. In the first column is given a reference number to the investigator's names and places of publication,—directly below the table. Columns *a*, *b*, *c*, and *d* give the name, formula, molecular mass, and the latent heat of vaporization, respectively of the liquids in question. The sixth (*e*) column contains the value of the expression $\frac{\mu\rho}{T_{abs}}$, and the seventh (*f*) the value of twice the natural logarithm of the pressure. (The pressure in the case of such liquids as have had their vapor tension determined is generally set as equal to that of the saturated vapor at 0°; for the others, the pressure has been put at 60^{mm} of mercury, as Jahn, in his experiments, reduced the pressure to this point before allowing evaporation to take place, and the others examined by him have not been investigated thoroughly as regards their vapor tensions. The pressure is reduced to absolute measure by multiplication by 13·6.) The last column gives the value of Le Chatelier's relation (17), obtained by adding the values found in columns *e* and *f* for each liquid.

TABLE II.

Ref. No.	Name.	Formula.	Molecular Mass.	Latent Heat.	$\frac{\mu\rho}{T_{abs}}$	2 log p.	
	a	*b*	*c*	*d*	*e*	*f*	*f* and *e*
I	Benzene	C_6H_6	78	107·6	30·75	9·8	40·55
II	"	"	78	109·0	31·14	9·8	40·94
II	Chloroform	$CHCl_3$	119·4	67·0	29·20	12·85	42·05
II	Carbon tetrachloride	CCl_4	156	52·0	29·25	12·21	41·46
II	Carbon disulphide	CS_2	76	90·0	25·00	14·92	39·92
III	" "	"	76	89·5	25·09	14·92	40·07
III	Ethyl ether	$(C_2H_5)_2O$	74	93·5	25·21	15·67	40·87
II	" "	"	74	94·0	25·49	15·67	41·16
I	Ethyl formiate	$C_3H_6O_2$	74	113·25	30·69	9·8	40·49
I	Propyl formiate	$C_4H_8O_2$	88	105·37	33·96	9·8	43·76
I	Methyl acetate	$C_3H_6O_2$	74	113·86	30·86	9·8	40·09
I	Ethyl acetate	$C_4H_8O_2$	88	102·14	32·92	9·8	42·72

I, Jahn, Zeitschr. f. phys. Chem., xi, 790, 1893.
II, Regnault, Memoires de l'Académie, xxvi, 761, 1862.
III, Winkelmann, Wiedemann's Annalen, ix, 208 and 358, 1880.

Table II shows that, while it is impossible to speak of a constancy for the values contained in the sixth column, through the introduction of the pressure correction in equation (17) a value is found equal in mean to about 40·5; it is remarkable that such a constancy is to be found in the values, since no great amount of accuracy can be attributed to the determinations of the latent heat or of the pressure. If the pressure correction be applied to the determinations of the latent heats of vaporization carried out under or nearly under atmospheric pressure, the "constant" is found to become equal to *39·18*, since 2 log 760 equals 18·48; this value, as is to be expected, is very near to that found for the liquids under the circumstances given in table II; undoubtedly, approximately the same value for the expression would be found under other pressures and concurrent temperatures, although the data at hand are too meager to make it worth while to perform the necessary calculations. As a conclusion to all that precedes and as a prediction of all future experimental work on latent heats of vaporization, it may be stated that the relation deduced by Le Chatelier may be put equal to about 40·00, thus

$$2 \log p + \frac{\mu\rho}{T_{abs}} = 40{\cdot}00 \qquad (17 \text{ bis})$$

IV.

In accurate determinations of temperatures of ebullition, it is often necessary to make a correction for the variation of the pressure from the normal pressure of 760^{mm} of mercury. In

case the latent heat of vaporization of the liquid under examination is known, this correction is easily made by the application of equation (1), which gives in terms of latent heat, temperature, and volume, the change of the boiling point with the concomitant variation of pressure. But the latent heats of volatilization are known for only a comparatively small number of liquids. In this case, the "law" treated of in the foregoing sections is specially applicable. We know from what precedes that near atmospheric pressure

$$\frac{\mu\rho}{T_{abs}} = \text{const.}, \tag{A}$$

The "constant" varying slightly for different classes of liquids from an average value of 20·7, at least, for normal liquids. If we set for the "constant," the letter C, neglect the volume of the liquid in comparison with that of the vapor —which will introduce no appreciable error,—and substitute for T its equal $\frac{\mu\rho}{C}$, equation (1) becomes transformed into

$$\frac{dT}{dp} = \frac{v\mu}{C}. \tag{B}$$

If now, from the gas equation

$$v = \frac{2T}{p} \tag{C}$$

we take the value of $\mu\rho$ ($\mu\rho = V$ = a gram-molecule of saturated vapor), and set it in equation (B), we obtain the equality

$$\frac{dT}{dp} = \frac{2T}{pC}; \tag{D}$$

and if p be the normal pressure of 760^{mm}, we get finally

$$\frac{dT}{dp} = \frac{2T}{760\,C} = \frac{T}{380\,C}, \tag{E}$$

or

$$dT = \frac{T}{380\,C} \cdot dp. \tag{F}$$

By putting for C, that value of the constant found for the class of liquids to which the liquid under examination belongs (see page 359), and for T, the absolute temperature of ebullition, we may obtain with a very considerable degree of accuracy the desired correction, with the restriction, however, that the variation of pressure is but slight, that is, not over 50 millimeters of mercury.

Chicago, January 22d, 1895.

ART. XXXI.—*On the Double Halides of Cæsium, Rubidium, Sodium and Lithium with Thallium;* by J. H. PRATT.

IN previous investigations upon the double halides of trivalent thallium with the alkali metals, the salts of only potassium and ammonium seem to have been carefully studied. The only cæsium and rubidium salts that have been made are $Cs_3TlCl_6 . 2H_2O$ and $Rb_3TlCl_6 . 2H_2O$ described by Godfrey,* but in the present investigation the compounds of this type were found to have one instead of two molecules of water of crystallization.

The present research has been carried out very carefully and systematically in order to obtain as complete a series of double salts in each case as possible. The salts that have been made belong to four types, corresponding to those previously made with potassium and ammonium, and are as follows,

3:1	2:1	3:2	1:1
$Cs_3TlCl_6 . H_2O$	Cs_2TlCl_5	$Cs_3Tl_2Cl_9$	----------
	$Cs_2TlCl_5 . H_2O$	--------	----------
----------	----------	$Cs_3Tl_2Br_9$	$CsTlBr_4$
----------	----------	--------	$CsTlI_4$
$Rb_3TlCl_6 . H_2O$	$Rb_2TlCl_5 . H_2O$	--------	----------
$Rb_3TlBr_6 . H_2O$	----------	--------	$RbTlBr_4 . H_2O$
----------	----------	--------	$RbTlI_4 . 2H_2O$
$Na_3TlCl_6 . 12H_2O$			
$Li_3TlCl_6 . 8H_2O$			

For comparison, a list of the previously described double salts with potassium and ammonium is also given.

3:1	2:1	3:2	1:1
$K_3TlCl_6 . 2H_2O$	$K_2TlCl_5 . 3H_2O$	$K_3Tl_2Cl_9 . 1\frac{1}{2}H_2O$	$KTlBr_4$
$(NH_4)_3TlCl_6 . 2H_2O$		$K_3Tl_2Br_9 . 1\frac{1}{2}H_2O$	$KTlI_4 . H_2O$
$(NH_4)_3TlCl_6$			$(NH_4)TlBr_4 . 5H_2O$
			$(NH_4)TlBr_4 . 2H_2O$
			$(NH_4)TlBr_4$
			$(NH_4)TlI_4$

Several points of interest, already noticed in connection with double salts prepared in this laboratory, are well illustrated by the series of new compounds to be described. With cæsium, a more complete series of salts was prepared than with the other alkali metals; and there is also an increase in ease of formation and in number of salts, from the iodides to the chlorides. The salts, formed from the alkali metal with

* Landenberg's Handwörterbuch.

the lower atomic weight are generally more soluble in water, form in larger crystals and with more water of crystallization than those with higher atomic weight.

Preparation.—The double salts were prepared in each case by mixing solutions of the thallic halide with the alkali halide in widely varying proportions, evaporating and cooling to crystallization. With the bromides and iodides the conditions for obtaining the double salts were improved by the presence of a little free bromine and iodine.

The crystals, soon after forming, were removed from the solutions, quickly pressed between filter papers to remove the mother-liquor, and, with the exception of the sodium and lithium salts, allowed to stand exposed to the air for some time. The latter on account of their instability, were placed in tightly stoppered weighing-tubes as soon as they were free from the mother-liquor.

Method of analysis.—In determining thallium, the salt was dissolved in warm water and a slight excess of ammonium sulphide added to precipitate the thallium as thallous sulphide. This was filtered and washed with water containing a little ammonium sulphide. The precipitate was then dissolved in hot dilute nitric acid, the solution evaporated with sulphuric acid in a platinum crucible, and then heated to constant weight within a porcelain crucible over a small flame. The filtrate from the thallous sulphide precipitation, was evaporated with sulphuric acid, the ammonium salts driven off, and the residual alkali sulphate ignited in a stream of air containing ammonia. The halogens were determined as silver salts in separate portions, with the precaution of adding sulphurous acid in the case of the iodides to prevent loss of iodine in dissolving, and it was found to be necessary in all cases to use a large excess of nitric acid in order to obtain the silver halide in a pure condition. Water was determined by igniting in a combustion tube, behind a layer of dry sodium carbonate, in a stream of dry air and collecting it in a weighed calcium chloride tube.

3 : 1 Cæsium and Rubidium Thallic Chlorides, $Cs_3TlCl_6 . H_2O$ and $Rb_3TlCl_6 . H_2O$.—The cæsium salt is obtained, as a white precipitate, when 0·25 g. of thallic chloride is added to a solution of 50 g. of cæsium chloride. The precipitate dissolves somewhat slowly upon heating the solution and crystallizes out on cooling. The range of conditions is very narrow as 3 g. of thallic chloride to 50 g. of cæsium chloride give the salt, Cs_2TlCl_5. The salt is soluble in hot water, but $Cs_3Tl_2Cl_9$ crystallizes from the solution.

The rubidium salt has a much wider range of formation. It is obtained when 1·5 to 25 g. of thallic chloride are added to a solution of 40 g. of rubidium chloride. It is very soluble in

cold water but gives another salt, $Rb_2TlCl_5 . H_2O$ upon crystallization. Both salts are white as are all the chlorides with one exception. Two separate crops of each were analyzed with the following results:

	A.	B. I.	B. II.	Calculated for $Cs_2TlCl_5H_2O$.
Cæsium	48·44	48·05	48·33	47·84
Thallium	24·21	24·45	24·37	24·46
Chlorine	25·37	25·53		25.54
Water	2·74	1·97		2·16

	A.	B.	Calculated for $Rb_2TlCl_5H_2O$.
Rubidium		36·54	37·09
Thallium	29·02	29·65	29·50
Chlorine	30·99	31·17	30·81
Water	2·51	1·72	2·60

The cæsium salt was obtained in hair-like crystals, too small for measurement. The rubidium salt crystallized in thin plates having a rhombic outline. Under the microscope these showed an extinction parallel to the diagonals and in convergent light a bisectrix at one side of the field, with the plane of the optic axes at right angles to the longer diagonal, indicating monoclinic symmetry.

2 : 1 Cæsium and Rubidium Thallic Chlorides, Cs_2TlCl_5, $Cs_2TlCl_5 . H_2O$ and $Rb_2TlCl_5 . H_2O$.—The anhydrous cæsium salt is formed when 5 to 8 g. of thallic chloride are added to a somewhat concentrated solution of 100 g. of cæsium chloride, and the hydrous salt, when 8 to 15 g. of thallic chloride are added to a more dilute solution of 100 g. of cæsium chloride. The rubidium salt was observed when 1·25 to 18 g. of rubidium chloride were added to a rather concentrated solution of 30 g. of thallic chloride. The two hydrous salts are white and the anhydrous compound is pale green. The cæsium salts are readily soluble in hot water but the salt $Cs_3Tl_2Cl_9$ crystallizes from the solution. The rubidium salt recrystallizes unchanged from water. The following analyses were made upon separate crops.

	A.	B. I.	B. II.	Calculated for Cs_2TlCl_5.
Cæsium		40·46	40·17	41·07
Thallium	31·11	31·82	31·62	31·52
Chlorine	27·19	27·30	27·20	27·41
Water	·81		·81	

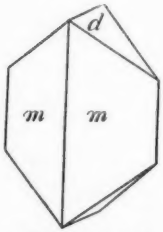
The small amount of water found in the above analyses, equivalent to about one-fourth of a molecule, was probably held mechanically by the crystals.

	A. I.	A. II.	B.	C.	Calculated for $Cs_2TlCl_5 . H_2O$.
Cæsium	40·03	39·84	40·30	39·85	39·97
Thallium	30·75	30·71	31·11	30·98	30·65
Chlorine	26·85		26·56	26·93	26·67
Water			2·88	2·37	2·71

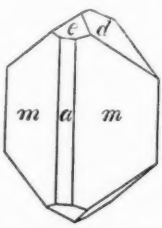
	A.	B.	Calculated for $Rb_2TlCl_5 . H_2O$.
Rubidium	29·09	28·97	29·97
Thallium	35·94	35·74	35·76
Chlorine	30·74	30·97	31·11
Water	3·34		3·16

The crystals of Cs_2TlCl_5 were in needles too small for measurement.

1.



2.



The crystallization of $Cs_2TlCl_5 . H_2O$ and $Rb_2TlCl_5 . H_2O$ is orthorhombic. The salts are similar in habit and are developed as in figs. 1 and 2. The forms observed are as follows:

a, 100	*d*, 011
m, 110	*e*, 102

The crystals of the cæsium salt were only about ·4 to ·6^{mm} in length, but the faces were smooth and gave good reflections on the goniometer. The axial ratio is,

$$\breve{a} : \bar{b} : \dot{c} = 0{\cdot}6762 : 1 : 0{\cdot}6954.$$

	Measured.	Calculated.
$d \wedge d$, $011 \wedge 0\bar{1}1$	*70°	
$m \wedge m$, $110 \wedge 1\bar{1}0$	*68 22′	
$m \wedge a$, $110 \wedge 100$	34 3 30″	34° 11′
$a \wedge e$, $100 \wedge 102$	62 51	62 44
$m \wedge d$, $110 \wedge 011$	71° 14′; 71° 16′	71 12
$d \wedge e$, $011 \wedge 102$	43° 9′	43 16
$e \wedge e$, $102 \wedge \bar{1}02$	54 6	54 32

Crystals of the rubidium salt were obtained from about 1·5 to 4^{mm} in length. The axial ratio is,

$$\breve{a} : \dot{b} : \dot{c} = 0{\cdot}6792 : 1 : 0{\cdot}7002.$$

	Measured.	Calculated.
$d \wedge d$, $011 \wedge 0\bar{1}1$	*69° 36′	
$m \wedge m$, $110 \wedge 1\bar{1}0$	*68 7½	
$m \wedge a$, $110 \wedge 100$	34° 4′; 34° 9′; 34° 5′	34° 4′
$a \wedge e$, $100 \wedge 102$	62° 52½′	62 49
$m \wedge d$, $110 \wedge 011$	71° 26′; 71° 23′	71 21
$d \wedge e$, $011 \wedge 102$	43° 19′	43 4½
$e \wedge e$, $102 \wedge \bar{1}02$	54 15	54 22

3 : 2 Cæsium Thallic Chloride, $Cs_3Tl_2Cl_9$.—The conditions under which this salt can be made are very wide, ·5 to 29 g. of cæsium chloride form a heavy white precipitate when added to a solution of 40 g. of thallic chloride. This dissolves readily in the solution upon heating and crystallizes in slender hexagonal prisms terminated by the pyramid. When the ratio of the cæsium chloride to the thallic chloride is 30 g. to 50 g. a salt is obtained which crystallizes in hexagonal plates. Analyses of the plates do not agree very closely with theory, but it is evident that they are the same as the prismstic salt with another crystalline habit. The high percentage of cæsium and the corresponding low percentage of thallium is probably due to the slight inclusions held by the crystals, which could be seen with the microscope. This salt is white, permanent in the air and recrystallizes unchanged from water. The analyses given below are of separate crops made under very different conditions.

	Cæsium.	Thallium.	Chlorine.	Water.
A	34·93			·65
B	35·09	35·64–35·51	28·09–27·99	
C			28·06	·95
D		35·63		
E	35·03	35·69	28·06	
F (Plates)	36·64	33·85	28·15	
G (Plates)	36·18	34·46	28·18	·61
Calculated for $Cs_3Tl_2Cl_9$	35·42	36·22	28·36	

The water found in these analyses was probably held mechanically by the crystals.

The prismatic variety of this salt showed only the forms of the prism, $10\bar{1}0$, and pyramid, $10\bar{1}1$.

Axis $c = 0{\cdot}82566$ $0001 \wedge 10\bar{1}1 = 43°\ 37'\ 50''$

	Measured.	Calculated.
$p \wedge p$, $10\bar{1}1 \wedge 01\bar{1}1$	*40° 21′	
$m \wedge p$, $10\bar{1}0 \wedge 10\bar{1}1$	46 21½; 46° 22′	46° 22′

Sections parallel to the basal plane show in convergent polarized light the normal uniaxial interference figure, with weak negative double refraction. The crystals served very well as 60° prisms for the determination of the indices of refraction with the following results:

	Red, Li.	Yellow, Na.	Green, Tl.
$\omega =$	1·772	1·784	1·792
$\varepsilon =$	1·762	1·774	1·786

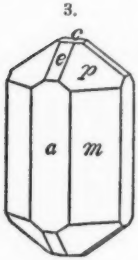
3 : 1 Rubidium Thallic Bromide, $Rb_3TlBr_6 . H_2O$.—This salt was formed, when 1·5 to 24 g. of thallic bromide were

added to a very concentrated solution of 50 g. of rubidium bromide. It crystallizes in beautiful golden yellow crystals, which are very soluble in water, giving the 1 : 1 salt on recrystallizing. Careful efforts were made to obtain a 2 : 1 and 3 : 2 rubidium thallic bromide, but without success. Several separate products, made under very different conditions, were analyzed with the results which follow :

	Rubidium.	Thallium.	Bromine.	Water.
A	28·57		49·29	2·49
B		20·39	49·66	
C	28·18	20·59		
D	28·03	20·16	49·42	
E	27·70	20·33	50·28	
F		20·64		
G	26·56	21·17	50·49	
Calculated for $Rb_3TlBr_6 . H_2O$	26·76	21·28	50·08	1·88

The somewhat high percentage of rubidium and the low percentage of thallium found in the first four analyses is probably due to the large excess of rubidium bromide in the concentrated solutions from which the crystals were obtained. As more thallic bromide was added, better crystals were obtained in more dilute solutions, which give percentages agreeing very well with the calculated.

3.



The crystallization of this salt is tetragonal. Doubly terminated crystals were obtained up to a length of 6mm.

The forms observed are :

a, 100 *m*, 110 *p*, 111
c, 001 *e*, 101

The habit is shown in fig. 3.

Axis $\dot{c} = 0{\cdot}80728$; $001 \wedge 101 = 38° 54' 45''$

	Measured.	Calculated.
$e \wedge e$, $\bar{1}01 \wedge 101$	*77° 49½′	
$a \wedge e$, $100 \wedge 101$	51° 6′; 51° 2′; 51° 3½′	51° 5½′
$a \wedge p$, $100 \wedge 111$	57 52; 57 54; 57 53	57 52
$e \wedge p$, $101 \wedge 111$	32° 5′; 32° 12′	32 8
$c \wedge p$, $001 \wedge 111$	48 51; 48 55	48 46
$m \wedge p$, $110 \wedge 111$	41 7; 41 4	41 13

The crystals show a weak negative double refraction.

3 : 2 Cæsium Thallic Bromide, $Cs_3Tl_2Br_9$.—This salt was observed, as yellowish red crystals, when 1 to 15 g. of thallic bromide were added to a solution of 50 g. of cæsium bromide. It was always obtained in small striated crystals, which were

not adapted for measurement. It is permanent in the air and recrystallizes unchanged from water. Analyses of separate products gave the following results,

	A.	B.	C.	D.	Calculated for $Cs_3Tl_2Br_9$.
Cæsium		26·52	26·14		26·13
Thallium	27·36	27·21	27·28		26·72
Bromine	47·24	47·14	47·08	47·27	47·15

1:1 Cæsium and Rubidium Thallic Bromides, $CsTlBr_4$ and $RbTlBr_4 . H_2O$.—These two salts are of nearly the same color, pale yellow. The rubidium compound which retains its luster and color much better than the other, recrystallizes unchanged from water, while the cæsium salt gives $Cs_3Tl_2Br_9$, when its solution is evaporated to crystallization. The cæsium salt was observed when 2 to 10 g. of cæsium bromide were added to 40 g. thallic bromide, and the rubidium salt when 3 to 24 g. of rubidium bromide were added to 40 g. thallic bromide. Analyses of several different crops gave the following results:

	A.	B.	C.	D.	Calculated for $CsTlBr_4$.
Cæsium	19·14			20·44	20·25
Thallium	32·36	31·79	32·04		31·05
Bromine	47·76		48·39	48·88	48·70

	A.	B.	C.	Calculated for $RbTlBr_4 . H_2O$.
Rubidium	13·77	13·41	13·91	13·63
Thallium	32·18			32·51
Bromine	50·06		50·30	50·99
Water	3·80			2·87

The crystallization of these two salts is isometric, the cube being the only form observed.

1:1 Cæsium and Rubidium Thallic Iodides, $CsTlI_4$ and $RbTlI_4 . 2H_2O$.—Both of these salts were prepared from solutions containing a large excess of thallic iodide and also from solutions containing a large excess of the alkali iodide, so that no other type of double iodides with these two metals could be obtained. As the thallic iodide was very difficultly soluble in water, alcoholic solutions were used where the thallic iodide was in excess. The salts are ruby red, with a brilliant luster, which is slowly lost in the air. Both are decomposed by water. The analytical results obtained from several different crops are given below.

	A.	B.	C.	Calculated for $CsTlI_4$.
Cæsium	16·57	16·38		15·74
Thallium	24·09	24·04		24·14
Iodine		59·48	59·67	60·12

	A.	B.	Calculated for $RbTlI_4 . 2H_2O$
Rubidium	10·34	9·78	10·26
Thallium	24·98	25·23	24·47
Iodine	60·38–60·32	60·79	60·94
Water	4·50		4·32

These salts crystallize in the isometric system, the habit being usually the cube truncated by the octahedron.

3 : 1 Sodium and Lithium Thallic Chlorides, $Na_3TlCl_6 . 12H_2O$ and $Li_3TlCl_6 . 8H_2O$.—Only one type of double salts could be obtained with these metals and it does not seem possible that others exist, for the ground was covered very carefully and systematically. On account of the extreme solubility of these salts, especially that of the lithium compound, the solutions had to be kept very concentrated, in a more or less syrupy condition, which accounts for the high alkali metal and low thallium found. These salts are transparent and colorless when first taken from the mother-liquor, but, upon exposure to the air, the sodium salt becomes opaque and the lithium compound deliquesces. Analyses of different products gave the following results:

	A.	B.	Calculated for $Na_3TlCl_6 . 12H_2O$.
Sodium	11·13	10·48	9·83
Thallium	27·79	28·39	29·06
Chlorine	31·23	30·45	30·34
Water		29·75	30·77

	A.	B.	C.	D.	Calculated for $Li_3TlCl_6 . 8H_2O$.
Lithium	3·71	3·79	3·73	3·78	3·61
Thallium	34·51				35·06
Chlorine	36·09	36·01	36·40	36·31	36·59
Water	25·14*				24·74

On account of the instability of the sodium and lithium salts no crystallographic determinations were made.

Repeated attempts to prepare lithium and sodium thallic bromides were entirely without success, hence no attempt was made to prepare the iodides.

The author wishes to express his indebtedness to Prof. H. L. Wells for valuable advice in connection with the chemical part of this work, and to Prof. S. L. Penfield for suggestions concerning the crystallography.

Sheffield Scientific School, December, 1894.

* By difference.

Art. XXXII.—*Argon, Prout's Hypothesis, and the Periodic Law;* by Edwin A. Hill.

If Argon be an element, its properties indicate that its place in the periodic classification is between F and Na, with an atomic weight of 20. Its non-metallic acidic electro-negative character, and low melting and boiling points, link it to Series 2 ending with F rather than Series 3 beginning with Na; just as Fe is more closely allied to Mn than Cu. Its resemblance to the members of transitional Group VIII, into which it would therefore fall, is shown in many ways. All the members of this group have high specific gravities, small atomic volumes, very weak chemical affinities, are inert, and with basic or acidic properties very weakly developed if at all. Argon is as truly transitional from Na to F as Group VIII in general is transitional between the two halves of Mendeléef's long periods, and belonging in a short period, is cut off from the other long period members of Group VIII by the same differences in boiling points, melting points, atomic volumes, specific gravities, and other properties, which separate the Series F, O, N, from Mn, Cr, V. To assign it an atomic weight of 40, thus usurping the place of calcium, and placing it among elements to which it bears no analogies whatever, would violate all the principles of the periodic law as now understood; and the great mass of accumulated evidence, upon which that generalization rests, requires us to accept any reasonable explanation of the supposed inconsistency, between the specific heat ratio of 1·66 and the diatomicity of the molecule, rather than the conclusion that it is monatomic.

That is to say the burden of proof is on those who oppose the conclusions drawn from the periodic law.

The argument for monatomicity, briefly stated, is this: The Argon molecule, if diatomic, being eccentric, would by molecular contacts acquire rotational energy, which it does not possess, as proved by the specific heat ratio; hence its molecule must be monatomic, and its atomic weight 40. The whole argument is based on the assumption that a molecular encounter involves an actual contact of atoms, or is of the nature of a collision between two elastic balls. This, however, is not a necessary assumption, nor was it Maxwell's view.* As pointed

* "I have concluded (he says) from some experiments of my own that the collision between two hard spherical balls is not an accurate representation of what takes place, . . . a better representation of such an encounter will be obtained by supposing the molecules to act on one another in a more gradual manner, so that the action between them goes on for a finite time during which the centers of the molecules first approach each other and then separate." And again: "We have evidence that the molecules of gases attract each other at certain small distances, but when they are brought still nearer they repel each other."

out by Thomson, Maxwell, and others, we need only postulate particles in motion, and a mutual action between them, tending to reverse that motion when they approach within certain small distances of each other, in order to arrive at all the ordinary conclusions of the kinetic theory of gases; which in its simplest form does not depend on any assumptions whatever as to the exact nature of the process by which the motion is reversed. It is only when Boyle's law no longer holds, that is when because of reduced volume the molecules are within the sphere of their mutual actions for an appreciable time, that the theory has to deal with the nature of the encounter, as in the case of viscosity, and for those conditions where we make use of Van der Waals' equation instead of the more simple form, $PV=RT$. But this ratio of the two specific heats in Argon, was determined under ordinary conditions of pressure and temperature, for which the gas obeys Boyle's law, hence in explaining this ratio we can without going counter to the ordinary kinetic theory of gases, make any assumptions we please as to the nature of the encounter and the constitution of the molecule, not at variance with known facts and the fundamental postulate of moving particles and reversed motion at small distances. Whenever we reach problems in any way conditioned by the nature of the encounter, the ordinary kinetic theory fails. Evidently the nature of the encounter is by it not properly taken into account. Maxwell, in order to test the theory as to viscosity found that, assuming the molecules to be hard elastic balls only acting on each other when in actual contact, viscosity should be proportional to the square root of absolute temperature, but assuming them to be systems repelling each other with a force varying inversely as the 5th power of distance, it should be proportional to the absolute temperature. As shown, however, by Barus and others, viscosity varies more rapidly than required by the first hypothesis, and more slowly than required by the second. Hence the encounter is not a mere collision involving an actual contact. Sutherland, says Thomson, concludes that the molecules *act without contact by a repulsive force* varying inversely with the fourth power of distance, and Pickering in his theory of solutions, represents chemical attraction to be due to charges on the surfaces of the attracting matter, but inalienable from the matter, *owing to a repulsive force* between the atoms similar to that which produces elasticity, preventing the atoms ever coming close enough together to allow of the charges combining by actual contacts. Now if we suppose the atom endowed with such a force of repulsion, varying inversely say as the fourth power of distance (following Sutherland) and combine this with the force of gravitation, then as the atom is approached the repulsive force

will first become equal to, and then greatly exceed the attractive force. Now conceive the atom, as enveloped by an imaginary spherical surface or shell, whose radius is the half distance at which these forces become equal, two such atoms would evidently act upon each other like perfectly elastic spheres of that radius; that is, they would strongly repel each other when separated by less than their imaginary diameter, and yet the atoms themselves if they have magnitude and are not mere Boscovitch points may be small as compared to their imaginary diameters, and so the approach of two such atoms might be checked and reversed without any actual contact between them.

Now the force which binds atom to atom within the molecule must do so in opposition to this force of repulsion, and if resembling (it is probably closely connected with) electrical attraction it would vary as the inverse square of distance, and two similar atoms drawn together by it to form a molecule would approach each other, until this force plus gravitation became equal to the force of repulsion. The stronger this attractive force the less the distance between the atoms of a diatomic molecule compared to the distance nearer than which two such molecules could not approach, which latter distance, as between two diatomic molecules, will be that at which the various attractions and repulsions are equally balanced (disregarding kinetic energy of translation which will tend to reduce this distance). Now when the force drawing the atoms together is large compared to that of gravity, the distance between the atoms within the molecule will be small compared with their least distance of approach, and the greater the difference between these quantities the less the action of atom upon atom, which is the action tending to produce internal rotations, and the closer will the action between two molecules during an encounter approximate to that of two repulsive forces concentrated at their respective centers of gravity.

Here we can apply the principle made use of in astronomy to simplify the problem of the three bodies in the case of perturbations, viz: That when the distance between two systems of bodies is large compared to the distance between their components, each system practically affects the other as if all its matter were concentrated at its own center of gravity. Evidently the nearer the approach to this condition (i. e. the stronger the force which aggregates the atoms within the molecule against the force of repulsion) the less the tendency to produce internal rotation.*

* The assumption here made is that the force of aggregation differs from gravitation and other forces, in what chemists refer to when they speak of an affinity being saturated or satisfied, thereby recalling the mutual saturation of the two

Says Professor Fitzgerald (discussing Lord Rayleigh's paper): "That the atoms in Argon may be very closely connected seems likely from its very great chemical inertness. Hence the conclusion from the ratio of its specific heats may be not that it is monatomic but that its atoms are so bound together in its molecule that it behaves as a whole as if it were monatomic."

And again (Dr. Armstrong): "It is quite likely that the two atoms exist so firmly locked in each other's embrace . . . that they are perfectly content to roll on together without taking up any energy that is put into the molecule."

A rigid mathematical analysis would unduly lengthen this paper but the principles involved are obvious. Some preliminary calculations which I have made show that if G = the force of gravitation, R = the force of repulsion, and d = any distance from the atom then

For d =	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{2}$	1	2	4	8
G–R =	−4032	−240	−12	0	0·188	0·058	0·0154

Showing how rapidly the repulsive force would increase at less than the imaginary atomic diameter ($d = 1$). At close distances theory requires that the repulsive should greatly exceed the attractive force, in order to produce rebound after impact, but at distances greater than the molecular diameter the attractive should be the greater force. This repulsive force evidently corresponds to that resisting compression in liquids and solids, and which at small distances from the surface is nil, but at the surface quickly becomes enormous in amount. Says Maxwell "It seems probable from the great resistance of liquids to compression that the molecules are at about the same distance from each other as that at which two molecules of the same substance in the gaseous form act on each other during an encounter."

A molecule composed of atoms of this kind, having no real surfaces in contact with those of other molecules during the encounter (friction eliminated) would act in a way tending to avoid internal rotation where solid elliptical or eccentric atoms would when in contact give rise to it. Thus A^1 A^2, B^1 B^2 being the atoms of molecules A and B during an approach, the distance A^1 B^1 between one pair of atoms would usually be less than between the other pair. When this distance was reduced to d, their approach would be very quickly checked, the distance A^2 B^2 almost as quickly reduced to d, the same value, and their

electrical fluids, Thus when two atoms are aggregated into a molecule by this force, it is thereby cancelled or saturated within the molecule, its energy becomes potential so to speak, and the force unlike gravitation, ceases to act on bodies without the molecule.

motion likewise checked, and the four repulsions would as to their tendency to produce rotation, be more or less balanced, with the tendency nil or very small in the case of one molecule, while in the case of the other, the tendency would depend partly on the circumstances of the encounter, but could not exceed a certain maximum value, depending on the ratio of the distance between the component atoms to d, the imaginary molecular diameter or least distance of approach. The greater this ratio the less the tendency for internal rotation. Now in a gaseous system as we would have all possible variations in the circumstances of the individual encounters, so also would we have all possible values of the internal rotations from the maximum value thus imposed, down to zero; but the average value of this rotation would be constant, and bear a fixed relation to the maximum value, and it would be this fixed average value which would determine the ratio of the translatory to the rotatory energy, so that a near approach of the ratio of the two specific heats to the value 1·66 would merely indicate that the distance between the atoms in the molecule was so small compared to their least distance of approach, that their mutual action on each other was the same as if all of their matter was concentrated close to their respective centers of gravity.

Now have we not here the explanation of that hitherto unexplained fact the varying values of this ratio which we find in diatomic gases? Thus the molecular gram of O^2, N^2, H^2, NO and CO has about 1·92 cals. of internal energy while that of Cl^2 and Br^2 has about 3·84 cals or twice as much. Ostwald's values are

H^2 and $N^2 = 1{\cdot}82$ $\quad$ $CO = 1{\cdot}86$ $\quad$ $NO = 1{\cdot}95$ $\quad$ $O^2 = 1{\cdot}96$
Cl^2 and $Br^2 = 3{\cdot}84$*

In Halogen Group VII strong chemical affinity for other elements would imply corresponding weakness in the force aggregating the atoms in the molecule, hence a greater distance between those atoms compared with their molecular diameter, therefore large atomic volume which we find to be the case, the volumes of the Group (VII) being comparable in size only with those of Group I where the same conditions apply with equal force; and Ostwald has said "The two conceptions of chemical affinity, stability on the one hand and activity on the other have been confused . . . Thus it is the chemically inactive bodies that are held together by the most powerful affinity, compounds which react with ease and rapidity can only hold their components loosely bound if at all."

* Ostwald gives a lower value for Br, but Regnault's specific heat determination leads to practically the same value (3.84) as for Cl.

If the views outlined are correct then the following relations ought to hold at least in Mendeléeff's short periods.*

Properties, etc.	Groups I and VII.	Groups III, IV, VIII.
Atomic volume	large	small
Tendency toward internal energy of rotation	"	"
Tendency to combine directly with other elements	"	"
Heat absorbed in separating atom from atom (dissociation)	small	large
Heat of formation in solution	"	"
Distance between the atoms in the molecule	large	small
Force of attraction for the atoms of other molecules	"	"
Distance between the atoms of different molecules	small	large
Force of attraction between atoms in the same molecule	"	"

How far does this scheme of properties conform to nature? In the two short periods Li—F and Na—Cl the atomic volume (distance between the atoms) decreases from alkali Group I to Carbon Group IV, and then increases from Nitrogen Group V to Group VII the Halogens. We are ignorant of the amount of internal energy of rotation in Groups I, II, III and IV but we have in Groups V, $N^2=1{\cdot}82$, in VI, $O^2=1{\cdot}96$, and in VII, $Cl^2=3{\cdot}84$. These values show the constant increase which the theory requires.

That the tendency for direct combination with other elements is a maximum in Group I decreases to Group IV and then increases again to Group VII is too well known to require illustration.

* Just as this article is going to press I note the following remarks made by Mendeléeff, March 14th, before the Russian Chemical Society:

"In favor of this supposition (monatomicity) we have the specific heat ratio at constant volumes and pressures, K, found by Rayleigh and Ramsay, to be near to 1·66, i.e. to the value which is considered as characteristic for monatomic gases. It must however be borne in mind that K varies for compound molecules, even when these last contain the same number of atoms; thus for most bivalent gases (nitrogen, oxygen, etc.) K is near to 1·4, while for chlorine it is 1·3. This last figure makes one think that K depends not only upon the number of atoms in the molecule, but also upon chemical energy, that is upon the stock of internal motion which determines the chemical activity of a body and the quantity of which must be relatively great with chlorine. If, with the chemically active chlorine, K is notably less than 1·4, we may admit that for the inactive argon it is much more than 1·4, even though the molecule of argon may contain two or more atoms."

Mendeléeff seems to lean toward the view that Argon is N^3 though prefers an atomic weight of 20 to one of 40 if it be a new element.

The data on dissociation are meagre. Iodine in Group VII as is known is easily melted and dissociated by heat, and probably also the alkali metals of Group I, while such bodies as C and Si of Group IV are but little affected, so that so far as known theory is again complied with; but more satisfactory conclusions can be drawn from the heats of formation in solution, for on the very probable theory, that in aqueous solutions of binary salts the elements are almost entirely dissociated, we can compare these thermal reactions of members of Series 3.

Na^2	Group I	$2(Na, Cl, Aq) = 193020$	Diff. $= -180840$
Mg^2	Group II	$2(Mg, Cl^2, Aq) = 373860$	Diff. $= -101790$
Al^2	Group III	$2(Al, Cl^3, Aq) = 475650$	
Si^2-P^2			
S^2	Group VI	$2(Na^2, S, Aq) = 208000$	Diff. $= +14980$
Cl^2	Group VII	$2(Na, Cl, Aq) = 193020$	

As the chlorides of Groups IV and V decompose instead of dissolve in water the series is broken. Now in the reaction $2(Na, Cl, Aq)$ we have the dissociation of Na^2 and Cl^2 and in $2(Mg, Cl^2, Aq)$ the dissociation of Mg^2 and Cl^4 that is to say the difference is the difference between the heat of dissociation of Na^2 and Mg^2 plus the dissociation heat of Cl^2. This term Cl^2 is a constant addition to the first two series differences. We are evidently justified in concluding that in Groups I and VII the heat of dissociation is small but large in Groups III and IV. We may however consider this series of heats of formation

Group I $2(Na, Cl) = 195380$, Group IV $2(Si, Cl^4) = 315280$,
Group II $2(Mg, Cl^2) = 302020$, Group V $2(P, Cl^5) = 209980$.
Group III $2(Al, Cl^3) = 321060$,

Here as before the result is masked by a constant addition depending on the constant increment Cl^2, but still the maximum values plainly are attained in families III and IV and the minimum in family I as the theory requires. "Substances," says Muir, "which are formed with the disappearance of heat are generally more readily decomposed by the application of outside forces than substances which are formed with the production of heat;" and Mendeléeff has noted the fact that elements of large atomic volume combine easily with others, and explains it by assuming a comparatively large distance between the single atoms in the molecule.

Our theory requires that the force holding the atoms together be large compared with both gravitation and the (elastic) force of repulsion. And there is evidence that this is so. For instance, at 18° Centigrade 2 grams of H and 16 grams of O, combined by the electric spark into 18 grams of water, give off 68360 calories of heat or more than 6 times the quantity necessary to raise the water thus produced from 18° to 100° and

vaporize it. Now the heat of combination is closely related to the difference between the forces binding H^2 to O and H to H and O to O, and if the heat of combination is large, the difference between these forces must be large, as also the forces themselves, compared with both gravitation and the force of elasticity or repulsion, for the latter will be of about the same order (at the least distance of molecular approach) as kinetic energy of translation. The fact that the energy of the motion of translation of the O and H molecules before combination is, as shown by Thomson, only about $\frac{1}{10}$th part of their total store, the great bulk of which must be potential, shows how great must be the forces binding the atoms together (upon whose differences the magnitude of the heat of formation depends), not only compared to gravitation but also to all other forces acting within the molecule.* The modern theory of electrolysis and salt solution postulates enormous electrical charges on the dissociated ions, which fully accords with the view herein expressed that the force of atomic aggregation is large compared to other forces. The intimate connection existing between valency, electrical character, chemical affinity and the electrons or charges on the ions has long been noted. The magnitude of these charges appears to be of the same order as the potential energy of chemical affinity, and as indicated by Ostwald, when valency is understood, so also will probably be all these other and closely related subjects.

Nature, in the edition of Feb. 7th, makes an apparently strong point for monatomicity when it states "that no diatomic gas has a specific heat ratio greater than about 1·42, and to place among them a substance for which the ratio is 1·66 would be entirely opposed to all other indications of a theory, which though admittedly only approximate, nevertheless in all other cases accords fairly well with the conceptions of the chemist."

It is notwithstanding a reasonable view, that when internal, vibrations are small (disregarding the higher order of vibrations which produce the lines in the spectrum) the tendency to split up into free ions will also be small. Chemical inertness goes naturally with the minimum of internal energy and atomic volume; and with practically no internal energy in Argon we ought to find it, just as we do, chemically very inert, so there are two horns to the dilemma. True if diatomic, Argon is the only diatomic gas known having so high a ratio for the two specific heats, but on the other hand if monatomic then its

* Mendeléeff remarks that 1 gram of H cooled to the absolute zero of temperature would evolve about 1000 units of heat and 8 grams of O half this amount, while in combining together they evolve more than thirty times that quantity, and hence the store of chemical energy must be much greater than the physical store proper to the molecule.

molecules are free ions, and what other instance have we of a chemically inert free ion? Which of the two horns shall we choose? The nascent state is par excellence the state of maximum tendency towards chemical combination, and finds its best explanation in the idea that the free and unincumbered ion is exceptionally prone to combination with the first partner it finds, but what have we about Argon, if monatomic, which in the slightest degree reminds us of the nascent state? Is not its great inertness just what we would not expect a free ion to possess? Which is the more unique, a diatomic gas without rotational energy or a free ion devoid of chemical affinity?

On the whole, therefore, it seems a fair conclusion as to Groups III, IV and VIII that the force binding the atoms together in the molecule is great, therefore their atomic volume is small, likewise the distance between the atoms in the molecule, their tendency to combine directly with other elements, and their tendency as diatomic gases to acquire internal rotation; hence the large quantities of heat required for their dissociation, and evolved when they are dissociated by solution in water or combine with other elements.

The theory on which these conclusions rest (which conclusions accord with the facts found) accords also with fact in that the resultant force causing the elements to combine in the free state to form a binary compound is not identical with that holding the atoms together after combination, which thing has proved a stumbling block to more than one theory of affinity, for certain forces may come into play to facilitate or restrain combination, as for instance the force required to dissociate the two component atoms, which are no longer factors in the problem after combination has occurred. The stability of the elementary molecule, the tendency to combine with other elements, and the stability of the compound, will in each case depend not on single forces, but will be determined by the magnitude of the resultant of many forces, changing in various ways and with varying conditions just as we find actually occurs in nature, as for instance in cases of reversed chemical action and many others which will occur to the mind at once.

We may then briefly sum up the matter as follows: The Periodic law places Argon if an element between F and Na with an atomic weight of 20; which law has been confirmed by such a mass of evidence that any reasonable hypothesis should be adopted rather than a theory inconsistent therewith.

While Argon may yet prove to be an allotropic form of nitrogen, yet the specific heat ratio of 1·66 is apparently even less consistent with a triatomic than a diatomic molecule, so that in either case it is in order to show that such a ratio does not

necessarily involve monatomicity.* The weak point in the assumption that it does, lies in the view taken that the molecular encounter involves actual contacts, which is not a necessary assumption in the kinetic theory of gases. That such contacts do not occur is shown by Maxwell's computations coupled with the experiments on viscosity. Moreover, Maxwell did not believe in this theory of the encounter, and both Sutherland and Pickering assume the existence of a repulsive force. The greater the force of aggregation, and the smaller the distance between the atoms compared to the imaginary molecular diameter or least distance of approach, the less the tendency for internal rotation as shown by the application of the astronomical methods used in the problem of the three bodies. In Groups I and VII we have the maximum of atomic volume, internal rotation, and chemical activity, combined with small heats of dissociation both in solution and otherwise, indicating a weak force of aggregation within the molecule. In Groups III, IV and VIII we have these properties reversed, small volume, little if any internal rotation, chemical inertness, and large heats of dissociation indicating a strong force of aggregation within the molecule; and the fact that the translatory energy of the H and O molecules before combination is only $\frac{1}{7}\frac{1}{6}$th of their total store of energy, which is not rotational and

*The evidence grows stronger that Argon may be Nitrogen with the molecular formula N^3, the theoretical density of which (21), would closely agree with that (19·9) found for Argon. There would then be more or less analogy between Oxygen O = O, Ozone $\begin{matrix} O \\ O-O \end{matrix}$, Nitrogen N≡N, and Argon $\begin{matrix} N \\ N=N \end{matrix}$. Thomson and Threlfall in 1886, observing a contraction in volume when the electric spark was passed through pure nitrogen, concluded that an allotropic form resulted; but Threlfall's later repetition of the experiment led to negative results. Johnson, from observations on the action of a hot tube upon Nitrogen also concluded that the gas can exist in two forms; one active, the other inactive. It has been recently remarked that as in Ozone, O^3, the characteristic properties (chemical activity) of Oxygen O^2 are enhanced; so in Argon, if it be N^3, the characteristic property of Nitrogen N^2 (its chemical inactivity) should also be enchanced; hence its very inert character. The boiling points seem to contradict this view. Oxygen—182·2°, Ozone—106·0°, Nitrogen—194·0°, Argon—187·0°. The two latter are almost the same, the two former widely separated; but Brauner (Chem. News, Feb. 15, 1895) has endeavored to explain this apparent inconsistency.

Quite recently Berthelot has succeeded in causing combination between Argon and the vapor of benzene, by means of the electric spark; thereby producing resinous compounds very similar to those produced, under like circumstances, by the action of benzene vapor on nitrogen.

In the formula $\begin{matrix} O \\ O-O \end{matrix}$ (Ozone) the molecule is apparently less eccentric than in O=O (Oxygen) and application of the principles already discussed will show, that its tendency for internal rotation should be less than in the case of oxygen. I know of no data as to the specific heat ratio for Ozone, but it would be interesting to know whether or not it is greater than in Oxygen. Evidently if Argon be N^3 we have here another principle tending toward small value of the internal energy, and a correspondingly large value in the ratio of the two specific heats.

hence must be potential, is only one of many similar facts proving that this force is very large as theory requires it to be, compared with the other molecular forces. Moreover, to call Argon monatomic, requires us to explain how a free ion, which should possess all the activities of the nascent state, can be as chemically inert as Argon has been shown to be.

In view therefore of the fact that the burden of proof is upon those attempting to prove monatomicity, it would seem safer at present to adopt some such way as this of explaining the supposed inconsistency between the specific heat ratio found and the diatomicity of the molecule, and follow the almost peremptory indications of the periodic law by accepting an atomic weight of 20.*

A very interesting question connected with the discovery of Argon, is what will be the effect of these researches upon Prout's hypothesis? Is it possible that Argon has been an unsuspected cause of error, which when properly allowed for will show the ratio of H to O to be almost exactly 1 to 16? This would make so many atomic weights even or half multiples of H as to render probable, what has been often surmised, the generation of the elements from a common form of matter (Protyle) by the continued addition of some one or more constant increments of mass. As pointed out by Mendeléeff the periodic law does not indicate continuous but abrupt variations of weight and properties, from family to family, corresponding to the changes in valency. Some years since I noticed the prevalence in the natural series of the elements of a regular alternation of intervals of 3 and 1 substantially as referred to by Dr. Gladstone in a recent issue of Nature.† Thus in round numbers and with a few changes we have the following series:

* There is, however, one real difficulty which it may be well to meet as far as can be done at present. As the atomic volume is the quotient of specific gravity into atomic weight we have these volumes: F=15? A=13·3 and Na=23·7, with the volumes of the metals of Group VIII varying from 6·7 to 9·2. Why then should not Argon have a volume approximately that of Group VIII, and since its volume is about that of F can we infer close aggregation in the Argon molecule in view of the known chemical activity of Fluorine?

We may say in reply that the volumes of Group I are about double those of Group VII, although their chemical activities (force of aggregation within the molecule) are about equal, thus we have these volumes: F=15.? Na=23·7; Cl=25·6, K=45·4; Br=26·9, Rb=56·1; I=25·6, Cs=70·6. Now Argon if transitional from F to Na should have its volume a mean value or about 19·5, whereas it actually has a volume of 13·3, the difference indicating the strong force of aggregation within the Argon molecule which the theory requires. That is, the force of aggregation, weak in F and Na is strong in Argon, and the repulsive force in Argon is a mean of that in F and Na with its value in Na about double that in F.

† Quite curiously in an article which I prepared on this subject but did not publish I almost duplicated Dr. Gladstone's remarks about this relation and its bearing on the atomic weight of Argon some days before his article was received in this country.

$$\frac{?}{0}3\ \frac{?}{3}1\ \frac{?}{4}3\ \frac{Li}{7}1\ \left(\frac{Be}{8}\right)3\ \frac{B}{11}1\ \frac{C}{12}3\ \left(\frac{N}{15}\right)1\ \frac{O}{16}3\ \frac{F}{19}1\ \frac{A}{20}3\ \frac{Na}{23}1\ \frac{Mg}{24}3$$
$$\frac{Al}{27}1\ \frac{Si}{28}3\ \frac{P}{31}1\ \frac{S}{32}3\ \left(\frac{Cl}{35}\right)1\ \frac{?}{36}3\ \frac{K}{39}1\ \frac{Ca}{40}3\ \frac{?}{43}1\ \frac{Sc}{44}3\ \frac{?}{47}1\ \frac{Ti}{48}3\ \frac{V}{51}1$$
$$\frac{Cr}{52}3\ \frac{Mn}{55}1\ \frac{Fe}{56}3\ \frac{Co}{59}1\ \frac{Ni}{60}3\ \frac{Cu}{63}1\ \left(\frac{Zn}{64}\right)3\ \frac{?}{67}1\ \left(\frac{Ga}{68}\right)3\ \frac{?}{71}1\ \frac{Ge}{72}3\ \frac{As}{75}1$$
$$\frac{?}{76}3\ \frac{Se}{79}1\ \frac{Br}{80}3\ \frac{?}{83}1\ \left(\frac{Rb}{84}\right)3\ \frac{Sr}{87}1\ \left(\frac{Yt}{88}\right)3\ \frac{Zr}{91}1\ \frac{?}{92}3\ \left(\frac{Nb}{95}\right)1\ \frac{Mo}{96},$$
$$3\ \frac{?}{99}1\ \frac{?}{100}3\ \frac{Ru}{103}1\ \frac{Ro}{104}3\ \frac{Pd}{107}1\ \frac{Ag}{108}3\ \frac{?}{111}1\ \frac{Cd}{112}3\ \left(\frac{In}{115}\right)1\ \frac{?}{116}3$$
$$\frac{Sn}{119}1\ \frac{Sb}{120}3\ \frac{?}{123}1\ \left(\frac{Te}{124}\right)3\ \frac{I}{127}1\ \frac{?}{128}3\ \frac{?}{131}1\ \frac{Cs}{132}3\ \frac{?}{135}1\ \left(\frac{Ba}{136}\right)3$$
$$\frac{La}{139}1\ \frac{Ce}{140}3\ \frac{Di}{143}, \text{ etc.}$$

I have, in the main, used the nearest whole numbers, bracketed those values that might seem forced, and inserted a few numbers (possible blanks) to complete the series.

There is, I think, some other law or laws besides this simple one, effective in the matter, but there are many things justifying the view that this ideal arithmetical series, which on the whole is so closely attained (all things duly considered) expresses the chief of perhaps several laws, all jointly effective in limiting the mass of the elements.

One of the strongest objections thus far to the use of round numbers in such atomic theories, as well as to Prout's hypothesis in general, has been the irrationality of the ratio of H to 0. Now Lord Rayleigh has shown that at 13° C. water absorbs 4 per cent of its volume of Argon and that gases handled over water in the usual way almost invariably become contaminated with the Argon held in solution. Moreover, it is quite likely that in reactions for the production of gases where water is used as a reagent (e. g. evolution of H by electrolysis of water or action of dilute acid on Zn), Argon contamination might result from the Argon so dissolved, and that such contamination once acquired, would not be removed by any ordinary reagents through which the gas was passed. A simple calculation will show that with hydrogen contaminated by only $\frac{4}{100}$ths of one per cent of Argon, the ratio H to O would be reduced from 1 : 16 to 1 : 15·879 which is about the latest values deduced from direct weighings of the two gases. And in those determinations based upon the synthesis of water, by passing H over red hot oxide of copper, with Argon in the water from which the H was evolved and contamination having occurred,

the Argon, unabsorbed by any subsequent reagents, might finally turn up dissolved in the water formed by synthesis, and if this water were saturated with Argon the effect on the ratio would be to reduce it from 1 : 16 to 1 : 15·98.*

Probably it will be difficult to handle gases over the water bath without the risk of such contamination. In the case, however, of density determinations it would seem advisable after the weighing to absorb the gas by suitable reagents, and then if any residual gas, Argon or any other, be found, to apply the proper correction to the weights already obtained; I believe that when this has been done the ratio of H to O will be found nearer to the value 1 to 16 than is at present supposed.

It would be interesting to go more deeply into the question of the laws governing the masses of the elements to which I have barely alluded, and to which I have given attention for some years past, but this paper would then be extended far beyond all proper limits. At some future time I may discuss this matter also.

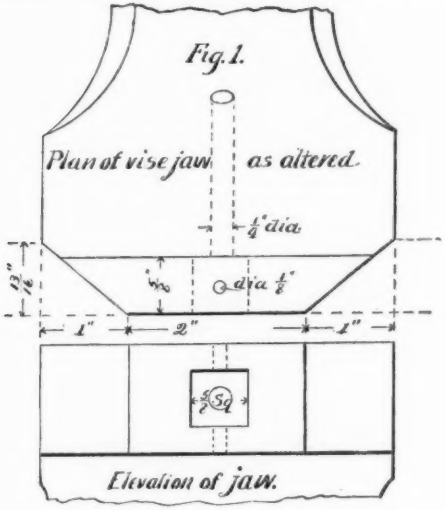
Art. XXXIII.—*An Improved Rock Cutter and Trimmer;* by Edgar Kidwell.

Over a year ago the Michigan Geological Survey required a rock cutter, and consulted me regarding the matter. I therefore designed one, and as a year's use has shown this cutter to be fully capable of doing the work required of it, a detailed description may be of value to those having need of a similar machine.

The cutter had to be suitable for heavy and accurate work, hence ample strength of parts, power in the mechanism, and freedom from lost motion were absolutely necessary. Previous experience in our shops had shown me that a No. 4 parallel swivel railway chipping vise, with wrought bar, as made by Merrill Brothers, possessed all these qualifications, and I therefore made in one of their vises such changes as were necessary to convert it into a cutter. The vise itself needed but few alterations, as it was necessary only to cut away the jaws to give the operator more room, and provide suitable openings for inserting the steel cutters. Provision was also made for holding cutters in place, and changing them quickly when necessary. Fig. 1 shows all necessary details.

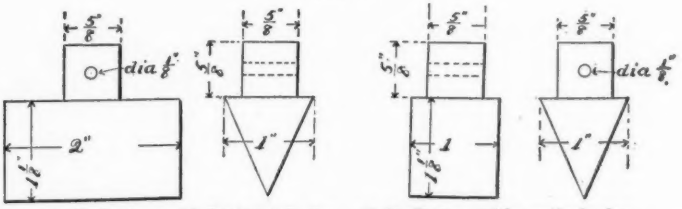
* It is rather significant that the best determinations by these two different methods closely approximate to these two values of 15·88 and 15·98 respectively.

Two forms of cutter were made, and a duplicate set of each was provided. The working drawings, fig. 2, show the details of cutters so clearly that further description is unnecessary. The specification required that these cutters should be of the



best quality Jessop's, Stubb's, or Mushet's steel, tempered very hard. It might be better for some kinds of work to have another form of cutter, with edges at an angle of 45° with top edge of jaws, but the two forms already mentioned have so far answered all requirements.

FIG. 2.



A, B, Cutters with horizontal edge. C, D, Cutters with vertical edge.

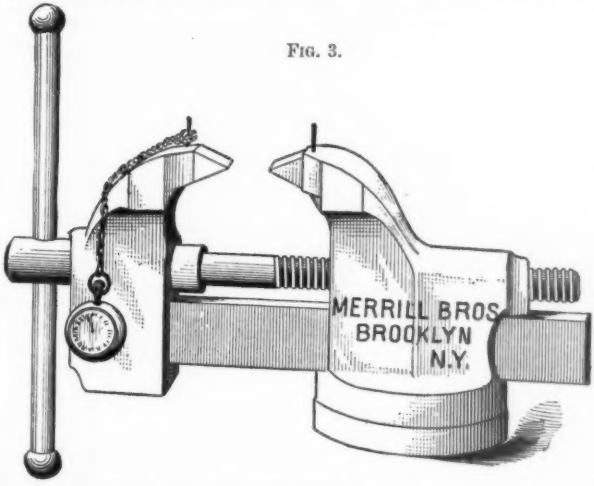
There should be also two pins, $\frac{1}{8}$" diameter, 2" long, for holding cutters; one pin $\frac{9}{16}$" diameter, 4" long, for removing cutters.

Unless a large amount of work is to be done, it will be advisable to order only a single set of cutters. This will make a material reduction in the first cost of the machine, and one set of cutters, if properly cared for, will last for years.

If very rapid work is desired any of the various forms of quick-acting vise might be employed as a basis for the machine, but I do not think the change would be a good one. The quick-acting vises are provided with weaker screws, and the parallel bars are invariably of cast iron, cored hollow, and sadly deficient in strength, hence a cutter made from a vise of this kind would be liable to complete collapse when used for heavy work. No matter what form of vise is used, if the machine is to be satisfactory it is absolutely essential that the screw be accurately cut, to prevent lost motion, and that each cutter be carefully fitted to its seat, shaped so that cutting edges will exactly meet when brought together, and be made of the very best tool steel, properly tempered. If these precautions are taken, the result will be a machine that is free from every trace of ricketiness, and amply able to stand up to any work that can be put on it. During the last year the Michigan Geological Survey has made with one pair of jaws from 2500 to 3000 cuts, on such specimens as conglomerates, sandstones, amygdaloids, traps, felsites, porphyries, silicified tufas, prehnite and datolite veinstone with copper, and its jaws show practically no signs of wear on the cutting edges.

Fig. 3 shows the machine ready for use.

FIG. 3.



In conclusion I would state that none of the features here mentioned are patented, and are free to all who may care to use them. The complete machine, from my drawings, can be got of Merrill Brothers, 465 Kent ave., Brooklyn, N. Y.

Michigan Mining School, Houghton, Michigan.

ART. XXXIV.—*Relation of the plane of Jupiter's orbit to the mean-plane of four hundred and one minor planet orbits;* by H. A. NEWTON.

ABOUT nine years ago (this Journal, III, xxxi, p. 319) I called attention in a brief note to the fact that the mean-plane of the orbits of the then known two hundred and fifty-one minor planets was inclined to the plane of Jupiter's orbit by a very small angle. In fact no minor planet out of the whole 251 had its plane so near to the mean-plane as did the planet Jupiter. Since that time we have added to the list of planets between Mars and Jupiter one hundred and fifty newly discovered ones, and it seems worth while to find whether the same relation of the large planet to the entire group of four hundred and one small ones holds true.

The plane of an orbit is determined by the longitude of the ascending node and the inclination, and its place may be represented to the eye by a plot in which the inclination is the radius vector and the longitude of the node is the polar angle. The point thus plotted is of course the pole of the plane.

The mean-plane of the 401 planes, regarding each plane as a unit, may be determined with sufficient accuracy for the present purpose by the formulas for computing the center of gravity of the 401 points plotted, viz:

$$401\, I \cos \Omega = \Sigma\, i \cos \Omega, \text{ and } 401\, I \sin \Omega = \Sigma i \sin \Omega :$$

where i and Ω are the inclination and longitude of ascending node of any orbit, and I and Ω are the same functions of the mean-plane of all the orbits. Computing I and Ω for the 401 orbits as given in the *Annuaire du Bureau des Longitudes* for 1895, adding three later orbits from the *Astronomische Nachrichten*, we have

$$I = 0°{\cdot}93, \text{ and } \Omega = 109°{\cdot}3.$$

The corresponding quantities for Jupiter are

$$i = 1°{\cdot}31, \quad \Omega = 98°{\cdot}9,$$

so that the inclination of the mean plane to Jupiter's plane is 0°·43. The three minor planets whose planes are nearest to the mean-plane are 1893 Y, (27) and (149). These planes make angles with the mean-plane severally equal to 0°·65, 0°·74, and 0°·77. The planet 1893 Y, was photographically discovered and has not yet a place in the numbered series of planets. Its plane will doubtless be much changed when the

orbit is definitely known, and it may or may not be found to be nearer the mean-plane than at present.*

The reason for the relation of Jupiter's plane to the minor planet planes is evident. The secular perturbation of the orbit of a minor planet by Jupiter is such that the inclination of the orbit plane is not greatly changed, but the node has a constant motion. The pole of the planet's plane therefore is constantly describing a curve, not widely departing from a circle, around the pole of Jupiter's plane. This motion is greater for some minor planets than for others. Hence whatever be the distribution of the poles at one epoch, the tendency of the secular perturbation by Jupiter is to finally distribute the minor-planet poles symmetrically around the pole of Jupiter's plane.

SCIENTIFIC INTELLIGENCE.

I. Chemistry and Physics.

1. *On the Presence of Argon and of Helium in Uraninite.*—At a meeting of the Chemical Society of London on March 27th, Ramsay announced that he had discovered both argon and helium in the mineral clevéite, a variety of uraninite. His attention was first called to this mineral by Miers of the British Museum, since Hillebrand had shown† that when treated with dilute sulphuric acid and warmed, the uraninite gave off two per cent or more of a gas which from the tests he applied to it appeared to be nitrogen. On sparking with oxygen however, in presence of soda, Ramsay found that the gas which he obtained from this mineral contained only a trace of nitrogen introduced probably during its extraction. In a Plücker tube its spectrum showed all the more prominent argon lines and in addition a brilliant line close to, but not coincident with, the D lines of sodium. Besides these there were a number of other lines, one in the green being especially prominent. Moreover argon obtained from the atmosphere shows three lines in the violet which are not to be seen apparently in the gas from clevéite. Hence the author suggests that possibly atmospheric argon contains some other gas in admixture, not yet separated, which may possibly account for the anomalous position of argon in its numerical relations with other elements. Further results are promised, especially in relation to the density of the mixture, a point of very great interest.

*If we consider the planes of the orbits of the eight principal planets, Jupiter's plane is not the nearest to the mean-plane of the system. But by omission of the plane of Mercury, the mean-plane of the seven other principal planets is a little nearer to Jupiter's plane than it is to any other planetary plane.

† This Journal, III, xl, 384, November, 1890.

At the same meeting, CROOKES reported upon the spectrum of this gaseous mixture from clevéite, two Plücker tubes containing it having been sent to him by Ramsay, the nitrogen in which had been previously removed by sparking. By far the most prominent line was a brilliant yellow one occupying apparently the position of the sodium lines. With higher dispersion, however, the lines remained single under conditions which would have widely separated the lines of sodium. Moreover, on throwing sodium light simultaneously into the spectroscope, the spectrum of the new gas was seen to consist almost entirely of a bright yellow line, a little to the more refrangible side of the sodium lines, and separated from them by a space a little more than twice that which separated the two components of the sodium line. This line appeared as bright and as sharp as D_1 and D_2. Careful measurements gave 587·45 as its wave-length; the wave-lengths of the sodium lines being for D_1 589·51 and for D_2 588·91. So that while the difference between the D lines is 0·60, that between D_2 and the new line is 1·46. It appears, therefore, that this line is the spectrum of the hypothetical element helium, discovered by Lockyer in the chromosphere of the sun and indicated as D_3. Its wave-length according to Ångström is 587·49 and according to Cornu 587·46. Besides this line of helium, there were seen traces of the more prominent lines of argon. Comparing the visible spectrum of the new gas with the band and the line spectrum of nitrogen, they were found to agree closely at the red and the blue ends, and to differ entirely between these points through a broad space in the green. The complete spectrum of the helium tube is as follows:

	Wave-lengths.		
(a) D_3 yellow	587·45	Very strong.	Sharp
(b) Yellowish green	568·05	Faint.	"
(c) " "	566·41	Very faint.	"
(d) Green	516·12	Faint.	"
(e) Greenish blue	500·81	"	"
(f) Blue	480·63	"	"

Photographs of this spectrum at first glance show in the violet portion, a close resemblance to the band spectrum of nitrogen. But a more careful examination shows that some of the bands and lines of the nitrogen spectrum are absent from the spectrum of the helium tube, while there are many fine lines in the latter spectrum which are absent from the spectrum of nitrogen. Measurements of these lines are in progress.—*Nature*, li, 512, March, 1895. *Chemical News*, lxxi, 151, March, 1895. G. F. B.

2. *On the Combination of Argon with Benzene vapor.*—By means of the silent electric discharge, BERTHELOT has succeeded in effecting the combination of argon with the vapor of benzene. The argon was received from Ramsay and had been circulated in the apparatus for the absorption of nitrogen until the nitrogen bands disappeared and there was no further contraction. The

density of the gas thus purified was 19·95 and the ratio of its specific heats was 1·65. Its volume was 37 cubic centimeters. In order to bring about the combination of argon with other substances, the author used the silent discharge, since he had found it, in his experience, much more effective than the spark in securing the permanence of unstable compounds. Thus nitrogen in presence of hydrocarbon vapors gives rise under these conditions to the most varied products of condensation—products, too, which decompose with elevation of temperature; while under the influence of the spark, hydrogen cyanide, because of its stability at high temperatures, is the sole product. Again the silent discharge, acting on a mixture of nitrogen and hydrogen, produces several per cent of ammonia, while the spark gives only infinitesimal quantities. Under the action of the silent discharge nitrogen reacts with water vapor to produce ammonium nitrite, a compound which, on standing, is decomposed at the ordinary temperature. Moreover the vapor of benzene was employed for the first experiment, because the author had found it very effective in the case of nitrogen. The apparatus used was that already employed in similar experiments (*Ann. Chem. Phys.*, V, x, 76–79, 1877), and the conditions were those described in the author's "Essai de Mechanique Chimique," the silent discharge being effected with the variable potential producible with an induction coil. With this apparatus the author had succeeded in bringing about the direct union of free nitrogen with hydrocarbons, carbohydrates and other organic substances. On submitting the mixture of argon and the vapor of benzene to the action of the silent discharge, combination took place though with more difficulty than in the case of nitrogen. The action is accompanied with a faint violet glow visible in darkness. In one of the five experiments there was finally formed a fluorescent substance which gave out a magnificent greenish light and afforded a special spectrum. A careful quantitative experiment, made with 10 c. c. of argon, yielded the following results: 100 volumes of this gas, put in contact with a few drops of benzene (by which its volume was increased about one-twentieth), was introduced into the discharge-tube and subjected to the discharge for ten hours under moderate tensions. After removing the benzene vapor by concentrated sulphuric acid, the remaining gas occupied 89 volumes; showing a condensation of 11 per cent. It was again mixed with benzene vapor and again subjected to the discharge, much higher tensions being employed. The diminution in volume was much more rapid, amounting in three hours to 25 per cent. The 64 remaining volumes was mixed anew with benzene vapor and again exposed for several hours to the discharge under still higher tensions. There remained 32 volumes of gas, consisting of hydrogen 13·5, benzene vapor 1·5 and argon 17·0 volumes. So that of 100 volumes of argon, benzene had condensed 83 into a state of chemical combination under the action of the silent discharge; or about five-sixths. The

quantity of the products was too small to permit of any extended examination. They resemble those produced by the similar action of the silent discharge on nitrogen mixed with benzene vapor and consist of a yellow resinous odorous substance condensed on the surface of the two glass tubes between which the electric action is exerted. Submitted to the action of heat this substance decomposes, yielding volatile products and leaving a bulky carbonaceous residue. The volatile products turn red litmus paper blue. Evidently therefore the conditions under which argon is condensed by hydrocarbons tend to affiliate it still closer to nitrogen. Indeed if it be permissible to increase its molecular mass from 40 to 42—which seems not unreasonable—this mass would represent one and a half times that of nitrogen; so that argon would bear to nitrogen the same reaction that ozone does to oxygen. Thus far, however, argon and nitrogen are not transformable the one into the other. Under the conditions now described it is evident that the supposed inactivity of argon ceases to exist.—*C. R.*, cxx, 581, March, 1895; *Chem. News*, lxxi, 151, March, 1895. G. F. B.

3. *On the Presence of Argon lines in the Spectrum of Atmospheric Air.*—In a communication to the Royal Society on February 21st, NEWALL has called attention to a line spectrum which appeared frequently upon the photographs of the air spectrum taken by him a year ago, and which he called "the low pressure spectrum." The lines of this spectrum were then unknown, but it now appears that they belong to argon, constituting seventeen out of the sixty-one lines of the air spectrum. To obtain this argon spectrum, a glass bulb was sealed hermetically to a Hagen-Töpler mercury pump, having a layer of strong sulphuric acid above the mercury. On reducing the pressure to $0{\cdot}14^{mm}$ (about 180 millionths of an atmosphere) a bright alternating discharge could be passed through the residual gas simply by surrounding the bulb with a coil of wire carrying the current from a condenser. After 30 minutes the pressure fell from $0{\cdot}13^{mm}$ to $0{\cdot}085^{mm}$ (from 174 $\overline{M}$ to 112 $\overline{M}$) and the photograph then taken showed the bands of nitrogen strong, mercury and nitrocarbon lines strong, hydrogen weak and no oxygen or argon lines. After thirty minutes more, the pressure has fallen from $0{\cdot}76^{mm}$ to $0{\cdot}015^{mm}$ (from 100 $\overline{M}$ to 20 $\overline{M}$) and in the photograph the nitrogen spectrum had faded considerably and a number of fine new lines appeared, constituting this "low pressure spectrum." Recent measurements show the practical coincidence of seventy-two lines belonging to this spectrum with the lines of argon as measured by Crookes. A table of the wave-lengths of these lines is given, with those of the red and blue spectrum of argon in parallel columns as given by Crookes. "It is interesting," says the author, "to find argon asserting itself unsolicited in quite new circumstances, and under conditions which practically constitute one more mode of separating argon from nitrogen—namely the getting rid of nitrogen by passing electric discharges through it in

the presence of hydrogen, or moisture and acid."—*Proc. Roy. Soc.*, Feb. 21, 1895: *Chem. News*, lxxi, 115, March, 1895.

G. F. B.

4. *On the Spark Spectrum of Argon as it appears in the Spark Spectrum of Air.*—On the 21st of March, HARTLEY read to the Royal Society a paper pointing out that certain lines obtained by himself and Adeney in 1884, in their photographs of the air spectrum, now appear to be due to argon. In their investigations, they used electrodes of aluminum, copper, platinum and palladium, and a condensed spark produced with a coil with a Leyden jar in circuit; the partial pressure—since argon constitutes about 1 per cent of the atmosphere—being about $7{\cdot}5^{mm}$. Since these are practically the conditions which as Crookes has shown give the brightest and purest spectrum of argon, the author thought it reasonable to expect the recognition of the blue and ultra-violet lines of this substance among some of the weaker lines in the spectrum of air. A table containing the wave lengths of 50 or more lines thus observed in the air spectrum is given in the paper, with the characteristic lines of the blue and the red spectra of argon in parallel columns for comparison. He considers of little importance the fact that argon gives two spectra; the red being apparently the spectrum of the first order or of the corresponding lower temperature, while the blue is the line spectrum at the higher temperature. "It is therefore more likely," he concludes, "that argon is one substance and not two. Whether it is a compound or an element is a question into which the following considerations may enter. There are at present no gaseous substances known which can withstand the temperature of the condensed spark without exhibiting the spectra of one or other of the elements of which it is composed. If therefore, argon were N_2 it would disclose the spectrum of nitrogen. As the spectrum is not that of any known substance it follows that if a compound, it must be a compound of a new element."—*Proc. Roy. Soc.*, March 21, 1895. (From advance sheets received from the author.)

G. F. B.

II. GEOLOGY.

1. *Reconnoissance of the Bahamas and of the elevated reefs of Cuba in the Steam Yacht "Wild Duck,"* January to April, 1893; by ALEXANDER AGASSIZ. 204 pp. 8vo, with 47 plates. Bulletin of the Mus. Comp. Zoöl. of Harvard College, vol. xxvi, No. 1.—The coral reefs of the West India seas may be regarded as the subject of Prof. Agassiz's Report, although only the Bahamas and Cuba are mentioned in the title. For, after the very full descriptions relating to the region of more special study, the report devotes 20 of its 200 pages to the coral reefs and banks of the Caribbean district, including therein the reefs of the north shore of South America, the Yucatan Bank and British Honduras. The origin of coral reefs is the concluding

subject. A brief review of the author's facts and conclusions have been given in volume xlv (p. 358) of this Journal, in a letter from the author. The many plates contain various contour maps, and views of reef regions, of æolian bluffs and rock, and illustrations of other subjects. Plate VIII is a colored contour map of the Caribbean Sea.

Prof. Agassiz, in discussing the origin of coral reef limestones, states objections to the subsidence theory of Darwin. Without touching here on the special arguments in its favor, two or three general facts may be stated.

In geological history, many limestones have been made exceeding 1000 feet in thickness which show by their fossils that they are not of deep water origin. Whether derived from coral and shell sediment like coral reef rock, or from shell sediment chiefly makes no difference; subsidence was required.

Subsidences of one or two scores of thousands of feet in depth have taken place in past time, over the region of the Appalachians, Alps, and other mountain regions; and in the sinking trough, sediments were formed successively at the water's level, or not far below it, to the thickness of the depth of subsidence; and some of the sediments were calcareous, making now thick limestone strata.

After the Cretaceous period, and in the Pliocene Tertiary chiefly, or the Tertiary and Glacial period, the whole region of the Rocky Mountains was elevated; the elevation was 16,000 feet in part of Colorado, 10,000 feet at least in the region of the Sierra Nevada, 10,000 feet in Mexico, and over 17,000 feet in British America, latitude, 49° to 53° and less to the north. The region of the Andes, at the same time, was raised to a maximum amount of 20,000 feet; the Alps, 12,000; the Himalayas, 20,000 feet. Moreover, at the close of the Champlain period there was another epoch of smaller elevation, introducing the Recent period. These elevations, affecting a large part of the continental areas, could not have taken place without a counterpart subsidence of large areas over the oceanic basin; profound oceanic subsidence was hence in progress during the growth of coral reefs. The subsidence cannot be questioned. J. D. D.

2. *Formation of Dolomite.*—C. KLEMENT, has a paper on the formation of dolomite in the "Bulletin de la Société Belge de Géologie, Paléontologie et Hydrologie," Volume viii, Brussels. 1894. In experiments, proceeding on the ground that the calcium carbonate of corals is in the state of aragonite, he digested in a covered platinum capsule, at a temperature of 90° to 92° C., finely pulverized aragonite, with a concentrated solution of common salt and magnesium chloride and sulphate in the proportions occurring in sea-water.

In his several trials he obtained a compound containing, besides lime and carbonic acid, 15 to 32·5 per cent. of magnesia, corresponding to 31·5 to 68·3 per cent. of magnesium carbonate. During the operation, the solution employed was gradually con-

centrated even to an abundant deposition of common salt. On account of the minuteness of the crystals, he was not able positively to prove their rhombohedral character, but believes that there is little doubt of this. The author deduces from his experiments, that the massive dolomite limestones have been produced in closed lagoons along a sea bottom through the action of the sea-water, concentrated by the sun's heat, on coral-made sediments, conforming, as he says, to Dana's views on Dolomization.

It should be here understood that Dana has never supposed that the dolomized calcareous sediments were always, or generally, those of coral reef origin; but that any calcareous sediments, whether from shells or corals, or any other source, would undergo the chemical change, under the conditions stated. It is important, therefore, to note that the shells of most Gastropods and Cephalopods, and the inner pearly layer of many Lamellibranchs, are aragonite; and that such shells contribute to the material of coral reef rocks, as well as to ordinary limestones. J. D. D.

3. *On Dolomite-making and dolomitic calcareous organisms.*—Under this title, A. G. Högbom, of Stockholm, discusses (Jahrb. f. Min., Geol. und Pal., 1894, vol. i, p. 272), the question as to the origin of the magnesia of dolomitic limestones. He finds by analysis that the common incrusting Nullipores of coral reefs—species of the genus *Lithothamnion*—commonly contain a large percentage of magnesium carbonate. He gives the results of fourteen analyses—1 by himself, 9 by N. Sahlbom, 3 by R. Mauzelius, and 1 by J. Guinchard, and he deduces for the mean of the whole, 10 parts of magnesium carbonate to 100 of calcium carbonate.

Mr. Högbom also cites results from analysis of Bermuda corals, by G. Forsstrand, in which the amount of magnesium carbonate and calcium carbonate, was, for a *Porites*, 0·62 and 95·94; for an *Oculina*, 0·36 and 96·20; for *Millepora alcicornis*, 0·41 and 95·86; for another *Millepora*, 0·77 and 94·39; for the reef rock of the Bermudas, 1·64 and 95·43; for 10 species of shells of Gastropods and Lamellibranchs from the outer edge of the reef, 0·19 and 97·32; but for a fine mud of terra cotta color from the lagoon, 4·04 and 92·93.

The author concludes that the magnesia of dolomite has probably come from an organic source; and that consequently the hypothesis of Dana, which derives it from the sea-water of evaporating basins, appears to be unnecessary.

We add here some additional facts.

Damour, in 1850, published an analysis (Bull. G. S. de France, vii, 675) of a specimen from Bréhat, on the coast of northwestern France, which he called a *Millepora* (M. cervicornis), but also said it was one of the *Algæ*, and of concretion-like form. It afforded him 8·51 per cent of magnesium carbonate and 87·32 of calcium carbonate.

The common *Millepora alcicornis*, of the West Indies, afforded S. P. Sharples 97·46 p. c. of calcium carbonate with 0·27 of calcium phosphate and 2·54 of water and organic matters. (This Journal, III, i, 168, 1871). In his analyses of *Oculina arbuscula*, *Manicina areolata*, *Siderastrea radians*, *Madrepora cervicornis*, and *M. palmata*, he obtained no magnesia but in each some calcium phosphate. It is to be noted that other analysts have overlooked apparently the calcium phosphate.

Forchhammer, analyzing a mixture of corals, found about half a per cent of magnesium carbonate; but in the Alcyonarian, *Isis nobilis* 6·36 per cent, and *Corallium nobile* 2·1 per cent.

4. *Bahama Expedition of the State University of Iowa. Narrative and Preliminary Report;* by Professor C. C. NUTTING. 252 pp. 8vo, No. 1 and 2 of Vol. III of the Natural History Bulletin of the University.

This volume is an account of a cruise to the Bahama Banks and the islands in their vicinity, by the members of a class in Natural History of the Iowa University, with Professors Nutting, G. L. Houser and H. F. Wickham as the executive committee, in all a party of twenty-one. It proved to be eminently satisfactory, both personally and as regards accessions to the University collections.

The Report contains brief notes on some of the species dredged or otherwise collected, with several figures in illustration; but the final descriptions are to appear later, specimens having been placed in the hands of different specialists. The volume has great value to any who may plan such expeditions on account of the descriptions of its outfit, the information to be gathered from the experiences of the cruise, and many facts observed along the way. J. D. D.

III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *National Academy of Sciences.*—At the annual meeting held at Washington, April 16–19, Dr. Wolcott Gibbs, one of the original charter members of the Academy, was elected president for a term of six years, Professor Marsh, president for the last two terms, having declined to be a candidate. The Academy voted unanimously "That the thanks of the Academy be tendered to the retiring president for the zeal and ability with which he has administered, in succession, the offices of Vice-president and President of the Academy during a period of seventeen years." Prof. Alexander Agassiz was elected foreign secretary, and Prof. Asaph Hall, reëlected home secretary.

Three foreign associates, Professor R. Leuckart of Leipzig, Professor Julius Sachs of Würzburg, and Professor Sophus Lie of Leipzig, were elected; also four new members.

The Barnard gold medal was awarded by the Academy to Lord Rayleigh for the discovery of argon, and the Watson gold medal to Seth C. Chandler for his researches on the variation of latitude, on variable stars and for his other works in astronomy.

The president announced the death of Professor James D. Dana, one of the original members of the Academy, and appointed Dr. E. S. Dana to prepare the biographical memoir. The president also appointed a special committee to represent the Academy at the funeral.

The following papers were read:

A. AGASSIZ and W. McM. WOODWORTH: On some variations in the genus Eucope.

A. AGASSIZ: Notes on the Florida Reef. The progress of the publications on the expedition of 1891 of the U. S. Fish Commission Steamer "Albatross," Lieut. Commander Z. L. Tanner, commanding.

M. P. RAVENEL: On soil bacteria.

A. M. MAYER: A linkage showing the laws of the refraction of light.

M. CAREY LEA: On the color relations of atoms, ions and molecules.

R. S. WOODWARD: Mechanical interpretation of the variations of latitude.

S. C. CHANDLER: On a new determination of the nutation-constant, and some allied topics.

L. A. BAUER: On the secular motion of a free magnetic needle.

J. S. BILLINGS: On the composition of expired air, and its effect upon animal life.

TH. GILL: Systematic catalogue of European fishes.

E. D. COPE: The extinct Cetacea of North America.

G. BROWN GOODE: On the application of a percentage method in the study of the distribution of oceanic fishes; (A.) Definition of eleven faunas and two subfaunas of Deep Sea fishes; (B.) The relationships and origin of the Carribeo-Mexican and Mediterranean sub-faunas.

IRA REMSEN: On the two isomeric chlorides of ortho-sulpho-benzoic acid. On some compounds containing two halogen atoms in combination with nitrogen.

B. A. GOULD: Biographical memoir of Dr. Lewis M. Rutherfurd.

H. A. NEWTON: Relation of Jupiter's orbit to the mean plane of four hundred and one minor planet orbits. Orbit of Miss Mitchell's comet, 1847 VI.

2. *Penck's Morphologie der Erdoberflache.**—Professor PENCK has added in his Morphologie der Erdoberfläche another notable number to Ratzel's series of geographical handbooks. The numbers already issued include Ratzel's Anthropogeographie, Hann's Klimatologie, Boguslawski and Krümmel's Ozeanographie, and Heim's Gletscherkunde; all standard works on their respective subjects. Penck's contribution is fully up to the high quality of its predecessors.

The plan of the present work may be fairly inferred from an abstract of its table of contents, as follows:—The form and size of the earth; area of land and water, mean altitude of lands and depth of seas, volume of lands and seas; continents and oceans and their permanence. Land surfaces; weathering and denudation by wind, rivers, and ice; deformations of the surface. The forms of the surface; plains, hills of accumulation, valleys, basins, mountains, depressions, caverns. The sea; its movements, coasts, and bottom; islands.

Under most of these subjects, the processes of form production, and the forms thus produced are separately considered; the general accounts of denudation found in geological treatises not

* Morphologie dor Erdoberfläche von Dr. Albrecht Penck, Professor der Geographie an der Universität Wien. Stuttgart, Engelhorn, 1894. 2 vols. 8vo. 471 and 696 pp. Author and subject indexes.

serving the author's purpose in his special treatment of the land. Much of the book is therefore *Morphogenie*, rather than *Morphologie.* Throughout both volumes, the citations of geological and geographical literature are remarkably numerous, and must serve an excellent purpose to those who wish to carry their studies to original sources. W. M. D.

3. *Orbit of Miss Mitchell's Comet, 1847, VI;* by H. A. NEWTON. —The computation of a definitive orbit for the Comet 1847, VI, is the subject of a memoir by Miss Margarita Palmer, being her thesis presented for the degree of Doctor of Philosophy conferred on her in 1894 by Yale University. Her work is published in the Transactions of the Yale Observatory. She found that a hyperbolic orbit better satisfied all the observations than did a parabola, though the best parabolic orbit does not do great violence to the observations. The best hyperbola has an eccentricity of 1·0001727.

A cursory examination shows that the position of Jupiter for a few years before 1847 was such as to increase the eccentricity of the comet's orbit. Herr THRAEN has shown (*Astronomische Nachrischten*, No. 3249), that the action of Jupiter and other planets upon the Comet 1886, II, previous to its period of visibility was enough to explain a change from a parabolic orbit to the hyperbola demanded for that comet by the observations. It seemed worth while to compute the like perturbations for the Comet 1847, VI.

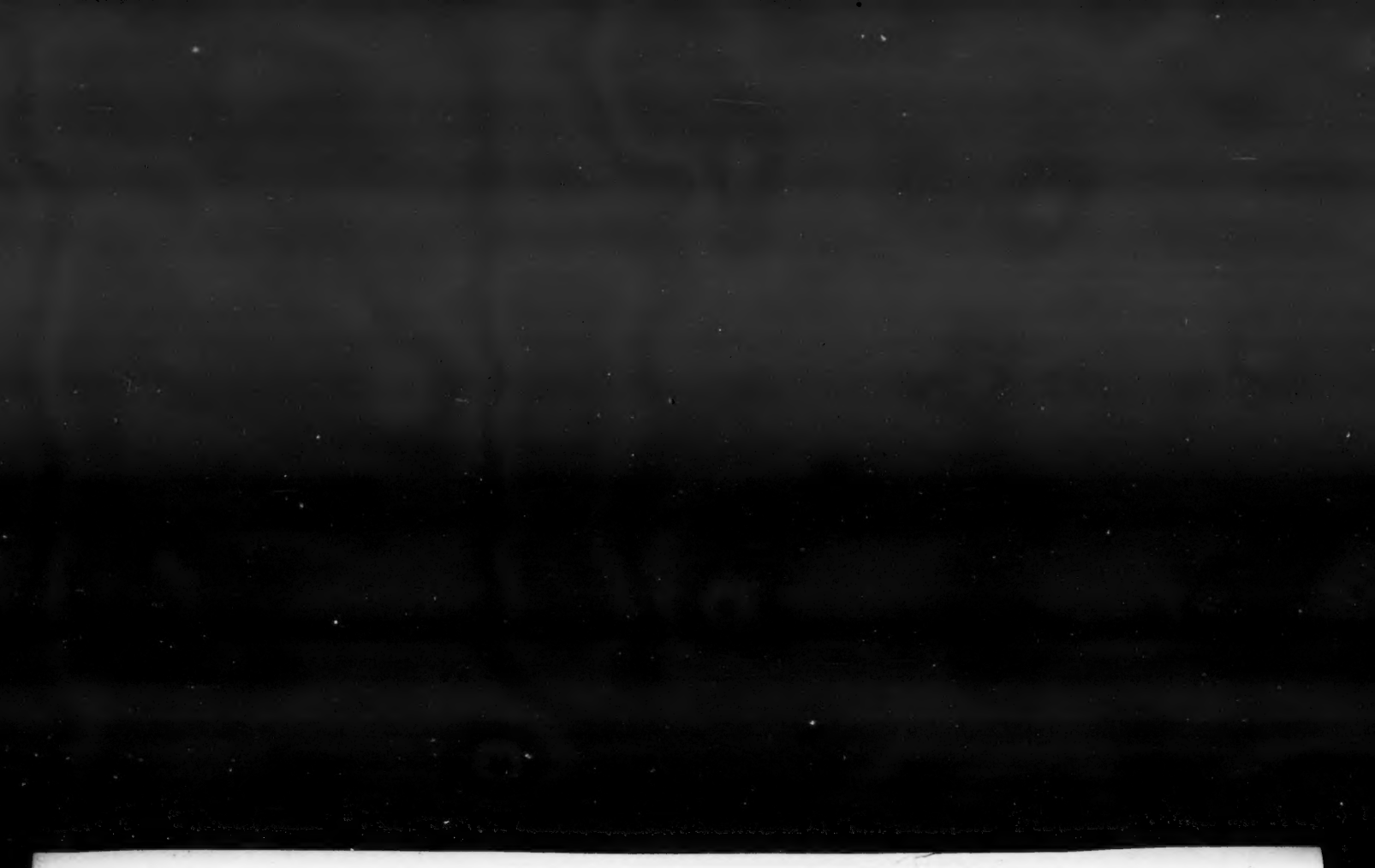
I find that from June, 1843, to November, 1847, the action of Jupiter and Saturn combined increased the eccentricity by ·000151. The action of Saturn was about one-thirtieth that of Jupiter. Previous to June, 1843, the action of Jupiter was to diminish the eccentricity of the orbit. Thus between February, 1838, and June, 1843, it changed the eccentricity by ·000034. During the whole period of ten years the change, therefore, was ·000117.

This explains so large a part of the computed excess of eccentricity over unity that it is fair to assume that a parabola to which these perturbations shall be applied would represent satisfactorily all the observations of the Comet 1847, VI.

OBITUARY.

DR. GIDEON E. MOORE of New York City died on April 13th at the age of fifty-three. He was a well known chemist, who had made some valuable contributions to the science, particularly in the line of mineral analysis.

PROF. JAMES E. OLIVER, the distinguished mathematician, who had been connected with Cornell University since 1871, died March 27. He was the author of a number of standard mathematical works.

FRANCESCO SANSONI, Professor of Mineralogy at the University of Pavia and author of many scientific papers, died about a month since.

It is announced in a recent number of "Nature" that the reported death of PROFESSOR H. WILD of St. Petersburg (see p. 328 of this volume), was happily a mistake, due to a confounding of similar names.